

Review article

A review on battery technology for space application

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ABSTRACT

This review article comprehensively discusses the energy requirements and currently used energy storage systems for various space applications. We have explained the development of different battery technologies used in space missions, from conventional batteries (Ag–Zn, Ni–Cd, Ni–H₂), to lithium-ion batteries and beyond. Further, this article provides a detailed overview of the current development of lithium batteries concerning their different electrode and electrolyte system, which needs special consideration for enabling their use for space application. This review also provides an outlook on the battery technology development for interplanetary space missions enlisting the research emphasis to be directed to meet the special energy requirements during various stages of such missions. This review is an attempt to provide a one-step comprehensive overview for any researchers, scientists, batteries manufacturers, and space agencies to first understand the current requirements critically and, accordingly, the solutions to prepare a future roadmap to develop highly efficient, next-generation advanced energy storage systems to mitigate the technical challenges and at the same time, minimizing the cost associated.

1. Introduction

After World War II, the Soviet Union established its missile programs and launched the first artificial satellite, “Sputnik 1,” into space powered by silver-zinc batteries [1]. Currently, nearly 98 space agencies [2] are working on space applications such as planetary exploration, meteorology, navigation, remote sensing of Earth's surface, providing global military forces with various warfare systems for air defense, telecommunications, and data transmission via satellites, etc. Besides, private companies (e.g., SpaceX, Blue Origin, Virgin Galactic) and other space agencies are starting to push space technologies for different applications such as space tourism, space-based power generation, the manufacturing of high-value materials in a microgravity environment, and the commercial development of extra-terrestrial resources [3,4]. In all this, an energy storage system (e.g., battery) with a primary energy source (e.g., photovoltaic) is a critical component of the spacecraft that ensures optimum operation and provides uninterrupted power coverage during the mission. The crucial aspects of achieving the mission goals of space science and exploration are energy and power storage to ensure

the longevity of their operations. Currently, the total energy source and storage system of the spacecraft requirements comprises nearly 28 %, directly related to the overall mission feasibility and cost.

There are three basic methods for energy storage in spacecraft such as chemical (e.g., batteries), mechanical (flywheels), and nuclear (e.g., radioisotope thermoelectric generator or nuclear battery) [5]. The operational length of the spacecraft of a mission, such as the number of science experiments to perform, the exploration of geological, terrestrial, and atmosphere, is dictated by the amount of energy provided by these energy storage sources. The specific energy of a flywheel is limited due to the tensile strength of the rotor material; therefore, this technology has never been used in space [6]. But it may have advantages in other space applications, such as low-Earth orbital missions requiring a re-usable energy storage capability of 5 KWh or more [7]. Primary and secondary batteries powered by photovoltaic or a nuclear radioisotope-based electric generator are mainly used as a space energy storage technology [7]. The critical role of these energy storages in the aerospace application is to provide power [8] (i) for satellites, extravehicular activities, planetary landers, and rovers during night-time or peak power

Abbreviations: NASA, National aeronautics and space administration; MER, Mars exploration rovers; AU, Astronomical unit; LLZO, Lithium lanthanum zirconium oxide; LNMO, Lithium nickel manganese oxide; LCO, Lithium cobalt oxide; NCA, Lithium nickel cobalt aluminum oxide; MCMB, Mesocarbon microbeads.

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operations; (ii) during launch and post-launch until the deployment of solar panels; (iii) for firing pyros and firing rockets for attitude control; (iv) during cruise anomalies or trajectory control maneuvers of the spacecraft; (v) to the spacecraft, its equipment, and payload during Sun eclipse periods; (vi) for night time or eclipse-time experimentation; (vii) for payloads, launch vehicles, and portable devices; (viii) for communication and data transmission; and (ix) to keep the electronics within a specified temperature range.

The energy storage system required for these missions largely depends on the particular type of space application. For instance, satellite batteries used in geostationary earth orbit (GEO) preferably require 180 cycles per year, whereas medium earth orbit (MEO) requires 5500 cycles per year. Jupiter and its moon's planetary mission require a power system that should be tolerant to high-intensity radiation, about 4 Mrad, of γ -radiation [9]. Contrarily, Mars and Venus's planetary missions require a power system that can operate under extreme temperatures, such as $-120\text{ }^{\circ}\text{C}$ low temperature for Mars and $475\text{ }^{\circ}\text{C}$ high temperature for Venus [10]. Thus, the selection of energy storage systems majorly depends on the type of mission (e.g., orbital, aerial, surface, or subsurface exploration), the environment being explored (pressure, temperature, radiation), and spacecraft functionality (e.g., orbiters, landers and rovers, and probes). Therefore, no single battery chemistry/system can fulfil all these complex requirements.

Different battery systems, such as primary, secondary, and nuclear batteries, are designed to meet these requirements. Here, the source of energy generation is a critical factor in selecting these energy storage (battery) systems. Nuclear batteries are usually preferred for the outer planets as these planets are away from the Sun, and the sun's intensity to produce power is insufficient. Contrarily, primary and secondary batteries charged with photovoltaic arrays are usually preferred for near planets where sufficient solar intensity is available to generate power with smaller arrays without a bulky system. The primary batteries used for space applications include Ag–Zn, Li–SO₂, Li–SOCl₂, Li–BC_x, Li–CF_x, and secondary rechargeable batteries are Ag–Zn Ni–Cd, Ni–H₂, and Li-ion.

In these battery systems, the Ag–Zn battery was used in the early days of space missions such as the Russian spacecraft “Sputnik” and the US spacecraft “Ranger 3” [11]. The advantage of the selection of the Ag–Zn battery was mainly due to its high specific power for long (600 W kg^{-1}) and short (2500 W kg^{-1}) duration pulses [12]. Currently, Ag–Zn battery chemistry is still being used for space applications such as thrust vector control, pyrotechnics, propulsion subsystem, and flight termination system (FTS) power. In 1960, the Ni–Cd battery became the most popular battery system for space applications which was used to provide power to the spacecraft for five years with $>30,000$ cycles requirements. Ni–Cd batteries were used in Solar Max and Landsat D Missions and were used initially for GEO spacecraft applications [13]. In 1980, the Ni–H₂ battery was used for the space application, which has almost two-time higher specific energy over the Ni–Cd due to the hydrogen electrode use over the cadmium electrode present in the Ni–Cd battery. Nickel hydrogen batteries are mostly explored for long-life operations such as 15 years with 60,000 partial depth-of-discharge cycles [11]. It is primarily used in GEO spacecraft missions such as Hubble Space Telescope, USAF, Intelsat V, etc. Nowadays, there has been a lot of use of Lithium batteries in space applications, including planetary missions, GEO and low earth orbit (LEO) spacecraft, and Lander and rovers because of their compactness, lightweight, and high specific energy and power density. Various developments in this battery system are ongoing, but these efforts mainly focus on portable electronics, electric vehicles, and grid applications. There is no particular attention to enabling their applications further for specific space application requirements.

To understand these requirements, let's first examine the various planetary missions carried out on different planets of our solar system. Emphasis is laid on the different battery chemistries as energy storage systems employed to overcome the operational challenges offered by the

atmospheric conditions of these planets to the spacecraft. A comprehensive overview of the various inner and outer planetary missions launched by the world's different space agencies, focussing on battery chemistries, is presented. Battery chemistries used for the extreme operating conditions in the missions directed to the exploration of natural satellites of various planets, extravehicular activities, and several spacecraft applications are also stated. In the next section, we focus on the technological development of different battery systems for space applications, namely primary and secondary. The development in the Li-ion-based rechargeable battery technology and beyond, including Li–S, Li–CO₂, and the nuclear battery, is enlisted and discussed in detail after that.

2. Classification of planetary missions

In this section, we have classified the application of batteries for space missions into six categories: (i) inner planet; (ii) outer planet; (iii) natural satellite; (iv) minor planet; (v) spacecraft (LEO, GEO, MEO); and (vi) extravehicular activity (EVA), as shown in Fig. 1.

2.1. Inner planet

The planets closer to the Sun, such as Mercury, Venus, Earth, and Mars, are considered inner planets. The human being as a habitat on earth, we shall discuss the other three inner planets as follows:

2.1.1. Venus

Venus's planet missions pose a significant challenge to energy storage systems due to its harsh condition, such as the average surface temperature of 723.15 K ($452\text{ }^{\circ}\text{C}$), the atmospheric pressure of ~ 92 bars (92 times greater than Earth), and the existence of corrosive environment (CO₂, CO, SO₂, and N₂) [14]. Furthermore, the use of photovoltaics for power generation is also not a promising approach because of the thick clouds present in its atmosphere that prevents sunlight from reaching Venus's surface and limits the efficiency of the solar cell (2 W/m^2) by 1000 times compared to the Earth (2000 W/m^2) [15]. Venus's orbital and aerial mission is more predominant than the surface mission as Venus's temperature is almost similar to that of the Earth's surface (at 65 km). However, the information obtained from orbiter or aerial missions is not optimistic, clearly revealed, and valuable because of the opacity of the Venus atmosphere, filled with thick clouds of sulfuric acid, CO₂, and other gases [16]. Contrarily, harsh ambiance with high temperature, CO₂ pressure, and corrosive environment condition limits the surface mission for a very short duration (2 h). Therefore, it is challenging to design and develop a surface lander with an appropriate energy storage system for long-term operation in such extreme conditions of Venus.

2.1.2. Mercury

Mercury has yet to be considered much for space missions because of its extreme temperature. During the daytime, the temperature reaches $427\text{ }^{\circ}\text{C}$, while at night, it falls to $-173\text{ }^{\circ}\text{C}$ [17]. This is due to no atmosphere to retain the heat. As it is also close to the Sun, spacecraft can be accelerated by the Sun's gravitational pull, and therefore spacecraft need additional fuel to de-accelerate during orbital insertion. Thus orbital, surface, and aerial missions would be even more demanding, requiring significant fuel expenditure and requirements.

Due to the harsh ambiance and extreme environmental conditions, Venus and Mercury have a more orbital and aerial mission (Fig. 2a shows the Venus and Mercury mission with an energy storage system) over the surface mission. Further, there are challenges to developing power source and energy storage technologies capable of extended operation on the Venus/Mercury surface. The rechargeable batteries will not work effectively on Venus's surface because of the limited solar energy available, which is not feasible for re-charging the battery. In contrast, Mercury has extreme temperature conditions (e.g., $427\text{ }^{\circ}\text{C}$ to $-173\text{ }^{\circ}\text{C}$). Developing rechargeable batteries in these harsh conditions is

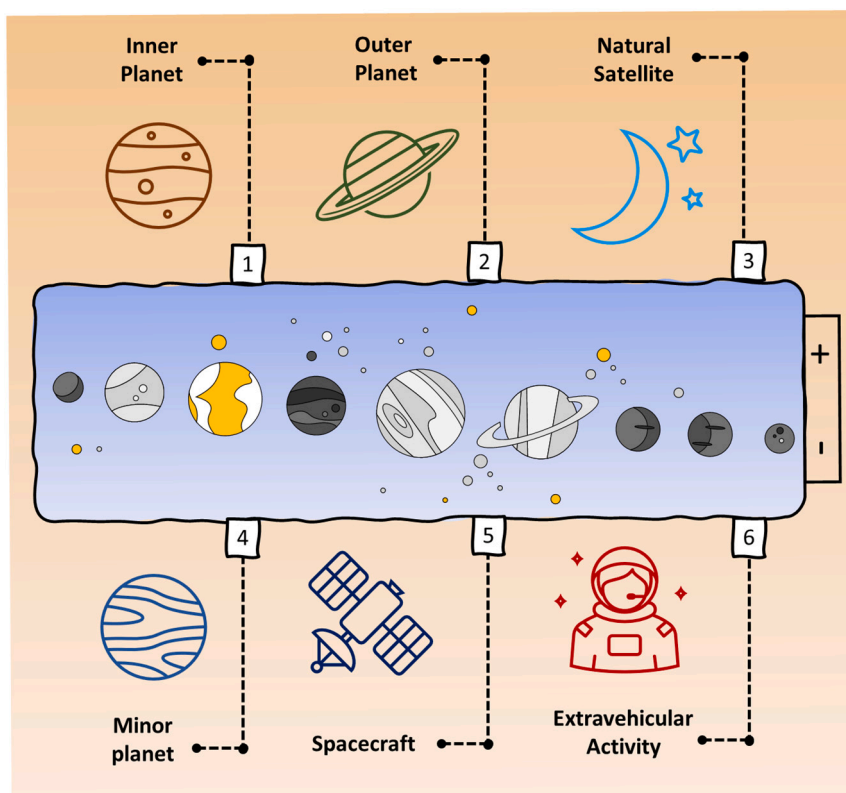


Fig. 1. Schematic showing the battery application for six categories of space applications discussed in this article.

very difficult. Therefore, primary batteries are the most viable solution for these missions in terms of high energy density and long life. Fig. 2b illustrates the various rechargeable and primary battery systems with operating temperature ranges [18]. The primary batteries, e.g., Li-MnO₂, LiSO₂, Li-CFx, and Li-SOCl₂, used a Li metal anode and organic/inorganic liquid electrolytes, which are unstable for high-temperature operation because lithium melts at 180 °C and organic/inorganic liquid electrolytes also vaporize at this temperature condition. Contrarily, rechargeable Li-ion batteries have a limited operating range of -40 to 65 °C due to liquid organic electrolytes use. Sodium-sulfur and sodium-metal chloride batteries can operate over 250–400 °C with high specific energy and long cycle life but must overcome safety concerns. However, Li-Al/FeS₂ batteries operate over 350–400 °C and utilize a Li–Al anode in LiCl–KCl eutectic melt and a FeS₂ cathode. Therefore, these battery systems can be adapted to the Venus/Mercury mission with considerable insulation, as used by previous Venus landers such as the Russian Venera series and Vega 2 [15].

2.1.3. Mars

The atmosphere of Mars is very thin, about 1 % of the earth's atmosphere, and consists of almost 95 % of carbon dioxide (CO₂) along with some inert gases like N₂, Ar, etc. Its thinner atmosphere and larger distance from the Sun make it a much colder planet than Earth and exhibit extreme temperatures throughout the Martian year. The average Martian temperature is -60 °C, and it can vary from -125 °C near the poles during winter to 20 °C during midday near the equator. The surface pressure of Mars varies (average 6 to 7 millibars) throughout the year, caused by a change in the amount of CO₂ gas in the atmosphere, which is <1 % of that of Earth [35,36].

Operation of rovers/landers on the Martian surface requires overcoming several operational barriers for the power system. Solar power is limited due to the distance from the Sun and the prevalence of dust storms. Martian surface temperatures vary widely, such as -80 °C on a summer night, -130 °C on a winter night, and 30 °C at the equator

(summer noon) [37]. These factors mean that power could be minimal and little thermal control available at times [38]. Therefore, Mars surface exploration missions pose several challenges for energy storage systems. These challenges include a) low-temperature operational capability (<-40 °C), b) long life capability, c) heat/radiation sterilization endurance, and d) high reliability. Other desirable features include low mass and volume. Furthermore, future Mars missions' energy storage system needs to depend on the type of spacecraft (orbital/aerial/probe/lander), as shown in Fig. 2c [8].

In the Flyby mission, the spacecraft movement is in the vicinity of the Mars planet without entering orbit and landing on the surface [39]. Here, unmanned space probes collect data by taking as many pictures of Mars [40]. The Mars orbiter's mission is mainly carried out for global mapping of the planetary surface and atmosphere which typically takes five years the mission. The planetary surface and atmosphere information such as the i) clouds and solar wind, ii) temperature on surface and atmosphere, iii) topography, composition, and physical properties of the surface, iv) measure magnetic fields, v) help to provide communications signals from the landers to the Earth. This Mars mission typically has five years and uses rechargeable batteries from nickel-hydrogen (Maven mission) to lithium-ion batteries (Mars orbiter mission). Generally, Mars orbiter batteries are operated and regulated above 0 °C. They need a long cycle life of nearly 30,000 cycles (there is a charge: discharge cycle once each orbit) at 10–30 % depth of discharge (DOD) [41].

In the case of a surface mission (lander and rover), the space agency NASA of the United States is the world's first to successfully deploy landers and rovers to Mars's surface. The spacecraft lander is a safeguarding shell that protects "Rover" and the airbags from impact forces. Rover is a device designed to move around and explore the solid surface of planets to collect information about the terrain and composition of the soil, dust, rocks, etc. It acts as a robot geologist that moves, operates, and communicates on the power, which comes from the energy stored in the batteries and multi-panel solar array [42].

The first rover, "Prop-M Rover" was launched by the Soviet Union in

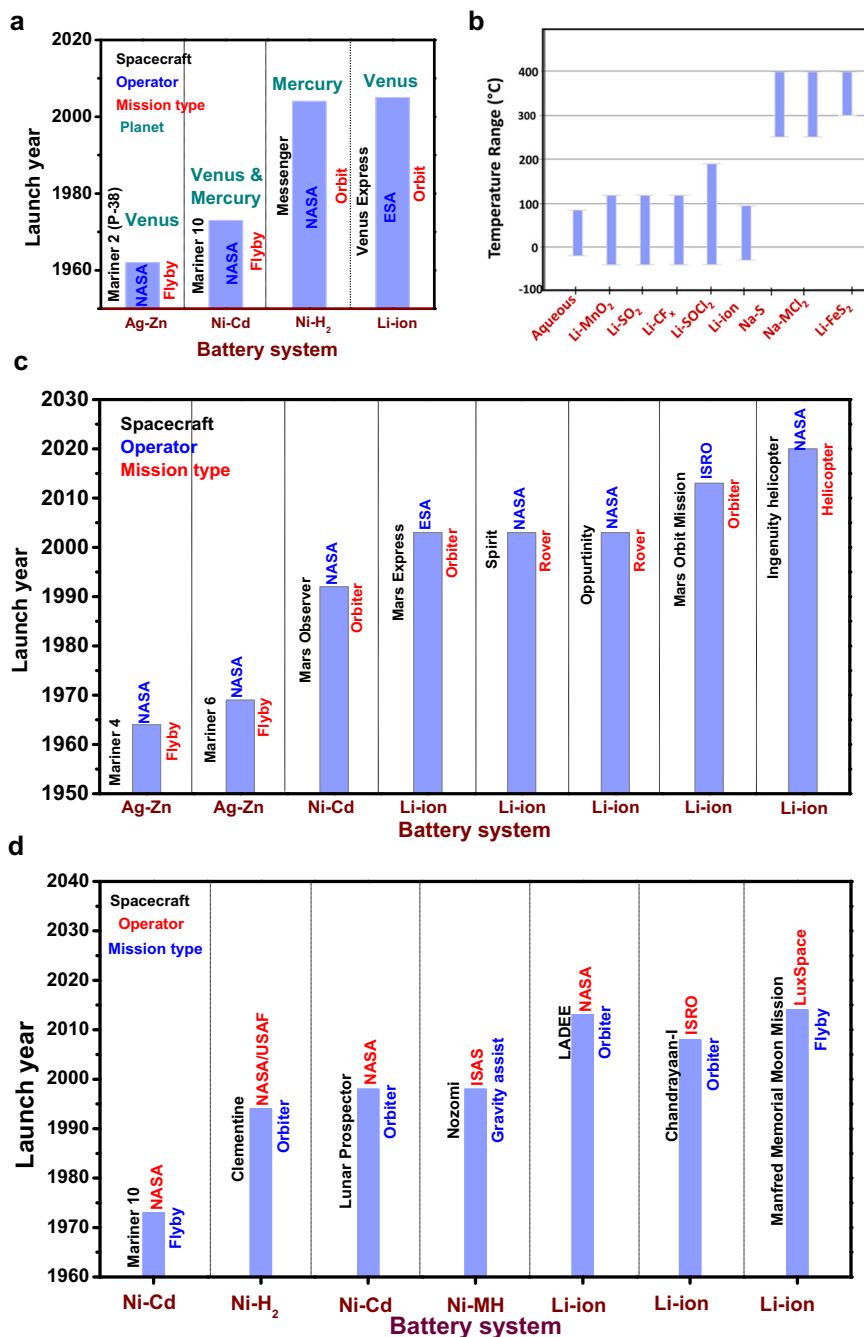


Fig. 2. a) Venus & Mercury planetary mission and battery system data collected from Ref [16,19,20]. b) Primary batteries for space application with their operating temperatures. c) Battery system utilized for Mars's mission; data collected from ref. [21–28]. d) Battery system used in Lunar mission; data collected from ref. [20,29–34].

1979, but it partially failed due to a communication problem because of a storm. After that, in 2004, NASA-Jet Propulsion Laboratory (JPL) landed three rovers, “Sojourner,” “Spirit,” and “Opportunity” on Mars. The landers and rover’s batteries operated at much lower temperatures (−30 °C), and battery performance at this lower temperature became a critical factor. However, battery cycle life is not high, with a maximum of 500 deep-discharge cycles at 100 % DOD compared to the orbital mission, which has 30,000 cycles. The MER mission uses three different primary, rechargeable, and thermal batteries [41,43]. The primary batteries are located on the Lander, which has a protective shell to carry the Rover while releasing it on the Martian surface. It's mainly used to support the entry, descent, landing operations, and initial deployments on Mars. This battery provides short-duration power (say, 1.25 h of

initial discharge at 15 A with 27.1 Ah capacity) and should have a high specific energy density, high discharge rate, low heat, and good shelf-life. The primary batteries mainly include Li-SOCl₂, Li-SO₂, and Li-BC_x; however, Li-SO₂ is considered the most promising system, considering its performance at high discharge rates, low-temperature operation, and the availability of technology [41].

The thermal batteries are located on the back shell and used for powering pyro and Entry, Descent and Landing (EDL) events such as the opening of a parachute during the descent phase of the mission, heat shield release, TIRS (Transfer Impulse Reaction System), and RAD (Rocket Assisted Descent) rocket firing [44]. Thermal batteries provide extremely high power for a short period and are activated by a high-current pulse, which generates a high temperature to melt electrolyte

Table 1
Lithium-ion battery performance characteristic for Mars's mission [45].

Parameters	Landers	Rovers	GEO	Planetary Orbiter
Capacity (Ah)	20–40	5–10	10, 20, 35	10, 20, 35
Voltage (V)	28	28	28–100	28
Discharge rate	C/5-1C	C/5-C/2	C/2	C/2-C
Temperature (°C)	–40 to 40	–40 to 40	–5 to 30	–5 to 0
Specific energy (Wh/kg)	>100	>100	>100	>100
Energy density (Wh/l)	120–160	120–160	120–160	120–160

pellets that further provide ionic contact between electrodes within the cell [45]. The Li-FeS₂ thermal battery was used in past Mars missions, such as Mars Pathfinder, Mars 98, and Mars Odyssey [41]. The rechargeable batteries used in the launch correct anomalies during the cruise and support surface operations (such as landers and rovers). Rechargeable batteries should have high specific energy, good low-temperature performance, low self-discharge, and high coulombic energy efficiencies. Further, the rechargeable battery should provide i) an operating voltage of 24–36 V, ii) energy of 220 Wh during launch, iii) energy of 160 Wh for supporting any fault-induced attitude excursion from the Sun point, iv) a cycle life of at least 270 cycles at 50 % DOD at 0 °C, and vi) multiple pulses of 30 A for 50 milliseconds, both at ambient and low temperatures. The rechargeable batteries such as Ni–Cd, Ni–H₂, Ag–Zn, and lithium-ion are used to meet these aerospace demands. Among these, Lithium-ion rechargeable batteries surpass the other rechargeable batteries in terms of mass and volume constraints, cycle life, and their ability to operate well at sub-zero temperatures (down to 30 °C) at moderate rates [41,45]. The desired performance characteristic of lithium-ion batteries for the Mars mission is summarized in Table 1.

2.2. Outer planet

There are four outer planets in our solar system Jupiter, Saturn, Uranus, and Neptune. Jupiter and Saturn are gas giant planets, whereas Uranus and Neptune are ice giants.

2.2.1. Jupiter

It is the giant planet in the solar system. Jupiter also has rings similar to Saturn, but Jupiter's rings are made of dust, notice. Jupiter's atmosphere has hydrogen and helium, an ocean identical to Earth but made of hydrogen instead of water [46]. On Jupiter, the pressure and temperature are about 0.1 bar and 110 K, respectively, from tropopause (approximately 50 km above the visible clouds) [47].

2.2.2. Saturn

Its atmosphere mainly comprises 18 to 25 % of helium and 2 % of other molecules, and the remaining is hydrogen and helium (18 to 25 %). In the troposphere, the temperature ranges from –130 °C to +80 °C [48], and at a pressure of 1 bar, it is –138 °C [49].

Whereas Titan is the largest moon of Saturn. Titan receives only 1 %

of sunlight as compared to the Earth. Therefore, the surface temperature on Titan is always chilly, about 94.15 K (–179 °C). Titan has an atmosphere of nitrogen similar to earth but has a surface pressure of 50 % higher. Titan also has clouds, rain, rivers, lakes, and seas, like Earth's, but contains liquid methane and ethane. However, Titan's subsurface (beneath a thick crust) contains liquid water rather than methane and could be a place for life [50].

2.2.3. Uranus and Neptune

These planets have similar masses and internal compositions but different bulk chemical compositions compared to Jupiter and Saturn. Uranus is a colder planet having a temperature of –224 °C compared to Neptune (–214 °C), despite Uranus being closer to the Sun. However, astronomers' hypotheses that Neptune has a higher internal temperature due to heat exchange between the core and outer layers this might be reason Uranus is colder than Neptune [51].

However, for these outer planet missions, we need batteries with the following requirements: (i) Jupiter encounters high intensities of radiation (which can potentially degrade polymeric materials); (ii) high impact resistance; (iii) ultra-low-temperature performance; and (iv) high levels of vibration and acceleration environments. However, the distance between the outer planets from the Sun is very far to generate power from the photovoltaic solar panels. It also requires more solar arrays, which will be too heavy and not feasible for the spacecraft. Therefore, past outer planet missions mostly used radioisotope thermoelectric generators (RTG), i.e., a nuclear battery that converts heat into electricity. In 1997, Pioneer 10 first mission was launched to the outer planet (Jupiter). This mission used SNAP-19 radioisotope thermoelectric generators (RTGs) as a power source that provided 155 W at launch and decayed to 140 W in transit [52]. Other missions also used RTG nuclear power sources (Table 2), such as Pioneer 10, Pioneer 11, Voyager 1, Voyager 2, Galileo, Ulysses, and Cassini–Huygens. However, the consistent development in photovoltaic (PV) technologies over the periods and simultaneously, the global shortage of plutonium-238 (a heat source of RTG) makes a photovoltaic power source with life rechargeable batteries economical, reliable, and preferable for outer planet missions [53]. Juno is the first mission to Jupiter, which used solar panels with lithium-ion batteries instead of RTG nuclear power source. However, solar power is only 4 % as intense as Jupiter compared to Earth's orbit [54].

2.3. Natural satellite

2.3.1. Moon (Earth)

Earth's moon "Lunar" has a hostile environment for landers and rovers because of its extreme surface temperature variation (+130 °C in the daytime to –170 °C in the night) because the ambient pressure of the lunar surface is a hard vacuum (no atmosphere) [64]. The orbit of the spacecraft is also affected by the lunar "lumpy" gravity as it has uneven mass distribution under its surface. Here, the batteries are required as power storage for satellite, rover, and human-crewed missions (Fig. 2d). The desirable battery characteristics for these missions include (a) high energy density such as 15 W to 15 kW for satellite, 90 W to 2 kW for

Table 2
Battery system utilized for different outer planet missions.

System Spacecraft	Jupiter	Saturn	Uranus	Neptune	Storage system
Pioneer 10 [55]	1973 flyby				RTGs
Pioneer 11 [56]	1974 flyby	1979 flyby			RTGs
Voyager 1 [57]	1979 flyby	1980 flyby			RTGs
Voyager 2 [58]	1979 Flyby	1981 flyby	1986 flyby	1989 flyby	MHW RTGs
Galileo [59]	1995–2003 Orbiter				RTGs
Ulysses [60]	1992, 2004				RTG
Cassini–Huygens [61]	2000	2004–2017, orbiter, 2005 Lander			RTGs
New Horizons [62]	2007				RTGs
Juno [63]	2016–2021 Orbiter				Lithium-ion

rover and 50 kW habitat for Manned mission, (b) high cycle life, (c) operating temperature of 0–40 °C for satellite and rover it's –233 °C in permanent shadow to in +183 °C in sunlight [65].

2.3.2. Europa (Jupiter)

Scientists think Europa has a liquid ocean of 40 to 100 miles underneath the 15 to 25 km of icy surface [66]. These oceans may have a water capacity, twice the Earth's all oceans combined, and there is a possibility that Europa's Ocean may be leaking out into space. The ocean could provide a promising place for life beyond Earth due to its interaction with a volcanic seafloor. However, their hostile environmental conditions, such as harsh radiation, low temperature (30K), and distance from the Sun (5 AU to 5.5 AU), create challenges for the energy storage system, spacecraft, and instrument hardware [67].

2.3.3. Enceladus (Saturn)

Enceladus is a small icy moon, only 504 km in diameter, hiding a global ocean of liquid salty water with small amounts of NH₃ and tholins [68]. However, like Saturn, it has a colder surface of a temperature of 75 K and an average temperature of 51 K. Enceladus Explorer (EnEx) mission deployed a Lander and orbiter equipped with the IceMole sub-glacial probe suitable to assess the existence of life on Enceladus [68].

However, a significant amount of energy is required to conduct such activities on the moon. As these moons are at a distance, negligible Sun energy reaches their surface, which is unsuitable for generating electric power using photovoltaic solar cells. From another perspective, a radioisotope power source is also not feasible due to the high radiation environments on the moon. The use of rechargeable batteries is also ineffective because it requires a charging source (such as a photovoltaic cell); therefore, using a high-energy-density primary battery is the viable solution for such a mission. F. Krause et al. [69] performed a feasibility study of existing Lithium primary batteries as power sources for deep space exploration. The selected primary battery chemistry, such as liquid cathode (Li/SO₂ and Li/SOCl₂) and solid cathode (Li/MnO₂, Li/CF_x, Li/CF_x-MnO₂, and Li/FeS₂), were tested for discharge at 0 °C and –40 °C, considering a low-temperature operation of the lander [69]. The Li/CF_x cells show the highest specific energy density of 640 Wh/kg and 508 Wh/kg (at 0 °C) for low (50 mA) and medium (250 mA) currents, respectively. At the same time, Li/CF_x cells were not capable of providing sufficient performance at a lower temperature (at –40 °C). This limitation was overcome by using a composite cathode of CF_x and MnO₂ electrode materials. At –40 °C, Li/CF_x-MnO₂ hybrid cathode cells showed the performance of 219 Wh/kg and 136 Wh/kg at low (50 mA) and medium (250 mA) currents, respectively [69]. However, at –40 °C, the highest specific energy density of 276 Wh/kg and 210 Wh/kg is provided by the Li/FeS₂ at the low (50 mA) and medium (250 mA) current, respectively.

2.4. Minor planet

Minor planets are small celestial/astronomical objects within the solar system that orbit around the Sun. They are mostly larger than meteoroids but smaller than the eight major planets [70]. They are also named mini planets, planetoids, or asteroids and include dwarf planets, trojans, centaurs, Kuiper belt objects, and other trans-Neptunian objects [71]. Energy storage system needs of the minor planet missions include a wide range of temperatures, operational capability, lighter-weight system (i.e., low mass and low volume), long operational life (>5 years), high specific energy, energy density, and long cycle life [72]. Spacecraft missions to minor planets are mostly flybys and powered with rechargeable batteries and RTG, as shown in Table 3. Galileo was the first spacecraft to explore an asteroid enroute to Jupiter, and at that time, solar panels and batteries were not technologically well developed for such long-distance missions. Therefore, it is powered by the two radioisotope thermoelectric generators (RTGs) through the radioactive decay of plutonium-238. In 1996, NEAR Shoemaker was the first

Table 3
Battery system used in minor planet mission.

Spacecraft	Launch date	Minor planet	Mission	Battery
Galileo [73]	1989	951 Gaspra 243 Ida	Flyby Flyby	RTG
NEARShoemaker [73]	1996	253 Mathilde	Flyby	Super Ni-Cd
Cassini-Huygens [61]	1997	433 Eros 2685 Masursky	Orbiter Flyby	RTG
Stardust [74]	1999	5535 Annefrank	Flyby	NiH ₂
MINERVA [74]	2003	25,143 Itokawa	Lander	NiH ₂
Deep Impact [75]	2005	(163249) 2002 GT	Flyby	NiH ₂
New Horizons [62]	2006	132,524 APL	Flyby	RTG
OSIRIS-REx [76]	2016	101,955 Bennu	Orbiter sample return	Li-ion

dedicated mission launched and designed by the Johns Hopkins University Applied Physics Laboratory for NASA to study the near-Earth asteroid, Eros. It's powered by gallium arsenide solar panels with a rechargeable super nickel-cadmium battery.

2.5. Extravehicular activities (EVAs)

The activity performed outside a spacecraft by astronauts when in space is called an extravehicular activity (EVA). The astronaut performed activity outside the vehicle or spacecraft by wearing a white suit called an extravehicular mobility unit (EMU). The spacesuit covers an astronaut's body and provides a protection and survival shield on the space shuttle and international space station [77]. Extravehicular activities include spacewalks to help build the space station, fix or repair something damaged, assist in capturing satellites in space, perform field science, emplacement science (i.e., geophysical and space monitoring) and technology demonstrations. These extravehicular activities can last as long as eight hours. Battery cells are used to provide primary power and energy storage to a different component of extravehicular mobility units, including fans, pumps, processors, controllers, valves, heaters, sensors for life support, electronics, processors for communications, and auxiliary equipment, such as lights and cameras [72]. The requirements of these batteries include high specific energy density, high specific power, operation over a wide range of temperatures, charging quickly (while an astronaut is taking a short break), and most importantly, human-safe operation [78].

There are two categories of battery used in EMU, one is 2000 Series Increased Capacity Battery (ICB) (e.g., Ag–Zn), and the other one is 3000 Series Long Life Battery (LLB) (e.g., lithium-ion). ICB is rechargeable for a minimum of 12 charge/discharge cycles with a life of 300 days, while LLB is also rechargeable for a minimum of 50 charge/discharge cycles over a life of 1825 days. The ICB and LLB performance requirements are shown in Table 4 [79]. NASA Glenn Research Center evaluated Lithium-iron phosphate cell chemistry performance for Lunar Extravehicular Activities. A123 Lithium iron phosphate cells can

Table 4
Long Life Battery (LLB) and Increased Capacity Battery (ICB) performance requirements.

Requirement	Long Life Battery (LLB)	Increased Capacity Battery (ICB)
Capacity at End-of-life	26.6 Ahr	26.6Ahr
Open circuit voltage (OCV)	16–21 V	16–21 V
Service life	1820 days (5 years)	300 days (<1 year)
Cycle life	>50 Cycles	32 Cycles
Mass	7.04 kg (15.5 lbf)	6.67 kg (14.7 lbf)

support an EVA with a 15-min recharge at 20 °C, but it cannot support 15-min recharge at −20 °C [78]. Lynntech designed hybrid system architecture and fabricated a fuel cell/Li-ion battery hybrid power supply for extended extravehicular activity (EVA) missions. This hybrid architecture has hybrid power sources, utilizing high energy density components in parallel with high power density components, which involve a proton exchange membrane (PEM) Fuel Cell/Li-ion battery and a rechargeable hydrogen storage unit. This unit overcomes safety and reliability issues with high efficiency and high power to weight and volume ratios for extended EVA mission requirements [80].

2.6. Spacecraft application

Battery powers required for spacecraft/satellites are mainly dependent on the satellite space placement/Earth orbit. The satellite is commonly launched in low Earth orbit (LEO), medium Earth orbit (MEO), and geostationary Earth orbit (GEO). The following section is discussed about the satellites placed in different Earth orbits and the types of battery power required for their operations.

2.6.1. Low earth orbit (LEO)

Satellites in low earth orbit (LEO) surround earth at a relatively low altitude of nearly 500–1500 km. This relatively small distance means there is a very small signal lag, usually about 0.05 s. These satellites are larger in operational than the MEO and GEO. It has been reported that SpaceX is launching nearly 12,000 satellites in the Starlink constellation in LEO for the development of low latency, broadband internet systems across the globe [76]. These satellites are used for satellite phones, data capability, and GPS communication. Here, satellites revolve in an either elliptical or circular orbit and complete their orbits in about one and a half-hour. During this period, satellites stay in the Sun for approximately 65 min and eclipsed for 35 min [11]. During Sun exposure, the battery gets charged, and during the eclipse stored power is utilized by the satellite. The one-year operation of these satellites required nearly 5000 (charge/discharge) cycles per year. Satellites in LEO usually operate for 4–5 years means they need >30,000 cycles [11].

2.6.2. Geosynchronous equatorial orbit (GEO)

A geosynchronous equatorial orbit is a high earth orbit that allows matching the orbital rotation of the earth; the satellite seems to stay stationary relative to the earth. GEO is located at an altitude of 22,236 miles (35,786 km) above Earth's equator and covers mostly the entire Earth's area for communication. Therefore, GEO is an ideal spot for monitoring weather, communications, surveillance, and earth observation (e.g., Meteosat and NOAA) [81]. The satellite in GEO is exposed to the Sun for 135 earth days followed by an eclipse of 46 earth days [11]. During Sun exposure, GEO spacecraft are required to harness the solar energy and store it in the battery. While during an eclipse the battery is used to provide power for the instrument loads as well as spacecraft communications. Over a year this will require 2 cycles of charge/discharge. The average duration of an LEO satellite is up to 15 years; therefore, we need a battery with a cycle life of nearly 30–40 cycle but should have a long calendar life for a long period of operation.

2.6.3. Medium earth orbit (MEO)

Medium earth orbit (MEO) satellites are located approximately 8000 miles from the earth's surface, and nearly 10 satellites can cover the entire earth area. Their orbit is mostly elliptic, and not circular. MEO satellite has a transmission delay of 0.25 s and is used for navigation, communication, geodetic/space environment science, and high-speed telephone signals. The orbital periods of MEO satellites range from 2 to 24 h. Telstar is the first satellite in medium earth orbit to provide high-speed telephone signals powered by nickel-cadmium batteries [82]. The main parameters required for the batteries to be used in LEO, GEO, and MEO missions are summarized in Table 5.

The selection of any battery system for the spacecraft application

Table 5

Battery parameters require for the LEO, GEO, and MEO missions [83].

Requirement	LEO	MEO	GEO
Lifetime (years)	2–15	Up to 18	Up to 180
Cycle per year	5500	90	180
Charge current (C-Rate)	0.33	0.07–0.1	0.05–0.1
Cycle depth-of-discharge (DOD)	10–40	60–80	60–80
Discharge current linked to cycle DOD (C-rate)	0.5–0.7	0.5–0.7	0.5–0.7
Temperature (°C)	0–40	10–30 eclipse season 0–30 solstice periods	10–30 eclipse season 0–30 solstice periods
Resistance to radiation	Low	High (crossing/proximity of Van Allen Belt)	High (crossing Van Allen belt)
Gravimetric energy density	Low	High	High

mainly depends on its specific (Wh/kg) and volumetric energy density (Wh/L) at a greater DOD and also the cycle numbers and calendar life of the battery. Sealed lead-acid batteries were mostly used for small satellites and experimental satellites. These satellites have low power requirements of 200 W or less with an operational life of two years or even less. They have the low-cost, high-rate capability but relatively low energy density and lower cycle life than sealed nickel-cadmium and nickel-hydrogen batteries [84]. Therefore, if the mission duration is expected to be more than two to three years and with a power requirement of 1–2 kW, Ni–Cd cells are mostly used because they are weight- and cost-effective for given power requirement and have a better packing efficiency than NiH₂. For example, experimental satellite MightySat, a Phillips Laboratory (PL) program, used Ni–Cd for their mission. Ni–H₂ battery has superior cycle life and high reliability over Ni–Cd and used with power requirements of 2 kW or greater. INTELSAT-V was the first commercial satellite to use NiH₂. However, the current power requirement for spacecraft application is mainly fulfilled by the lithium-ion battery due to its superior performance over the other battery, as shown in Fig. 3.

3. Different types of battery technology development for space application

This section is mainly focused on the different battery technologies such as primary, rechargeable (specially Li-ion battery in details), and nuclear battery for development/utilization for various space applications.

3.1. Primary batteries

3.1.1. Lithium-sulfur dioxide (Li-SO₂) batteries

Lithium-Sulfur dioxide batteries are employed when there is a requirement of moderate specific energy like powering planetary probes (Galileo, Cassini) or return capsules like Genesis; and the Mars Exploration Rover and Mars Lander [87]. In the Li-SO₂ system, lithium acts as the anode, while sulfur dioxide is the active cathode separated using a polymeric membrane with an organic electrolyte containing lithium bromide and sulfur dioxide dissolved in it. Li-SO₂ systems have a high OCP of 3 V and are suitable for operations in a temperature range of −40 to 60 °C [87]. It demonstrates specific energy of ~225 Wh/kg and is known to have the highest specific power among lithium primary cells [83].

3.1.2. Lithium-thionyl (Li-SOCl₂) batteries

Lithium-Thionyl (Li-SOCl₂) batteries are employed when there is a requirement of high specific energy but low specific power. These systems are preferred as primary battery power for long-tenure space

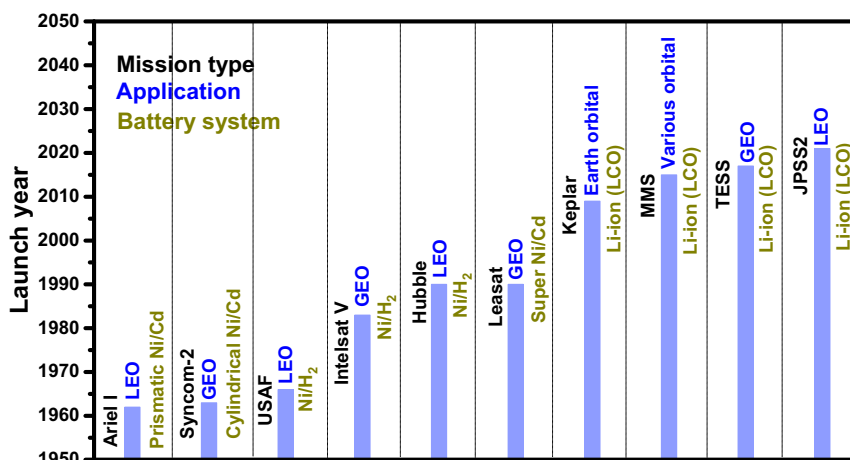


Fig. 3. Battery system used in LEO, GEO, and MEO missions; data collected from ref. [85,86].

missions. This system has powered the Mars Pathfinder Rover-Sojourner, Centaur launch vehicle, and Philae lander. In the Li-SOCl₂ system, lithium metal acts as the anode, while liquid thionyl chloride is the active cathode separated using polymeric membrane and thionyl chloride as the electrolyte containing tetra-chloroaluminate dissolved in it. The more details about Li-SOCl₂ chemistry system can be found in other reports [88]. The Li-SOCl₂ system has higher specific energy (390–410 Wh/kg) when compared to the Li-SO₂ system. The major limitation is its low specific power attributes (<100 W kg⁻¹). The other concerns about space missions are capacity fading at low-temperature operations (<-40 °C), uncertainty in radiation tolerance, etc., and thus require significant advancement [87].

3.2. Secondary batteries

3.2.1. Silver-zinc (Ag-Zn) chemistry

Silver-zinc chemistry exhibits the highest specific energy among the commercially available aqueous battery technologies [89]. Ag-Zn chemistry owing to its compact size, super discharge performance, and stable voltage is competent for short-lived launch vehicles. With the establishment of the space programs, Ag-Zn became the logical choice for powering critical units like the extravehicular mobility unit, the manned (Mercury, Gemini, Apollo), unmanned rocket or boosters (Delta 2, Atlas 2), the upper stages (avionic systems, Centaur), the get-away specials, etc.

The theoretical operating voltage of the cell is 1.5 V with specific energy >100 Wh/kg with a cycle life of 100–200 cycles during operation. Further details about the Ag-Zn battery can be access through other reports [90]. However, the Ag-Zn chemistry got locked out of the space missions' market primarily due to limited-service life (~2–3 years) and rapid degradation of performance capacity (limiting to 30–50 cycles), restricting its scope for futuristic space missions [91]. The other concerns involve the high cost, electrolyte leakage, and poor low-temperature performance (<-20 °C).

Recent advancements aimed to overcome the limited-service life and performance decay by modifying zinc anode, suppressing dendritic growth, electrolyte additives, etc. In a recent study by Liang et al. [92] demonstrated that the silver halide-zinc battery model involving simple addition of a mild electrolyte and anionic charging carriers into the battery system could achieve not only an enhanced cycle life of 1300 cycles (in contrast to <100 cycles of conventional battery) but also addressed the concern of cathode dissolution and dendrite formation. Lyu et al. [93] reported PEG-200 (polyethylene glycol, mol wt. 200) used as an additive in the alkaline electrolyte, which reduces the zinc dendrite formation and improves the cycle life to 100 cycles without fade in capacity. In the other study, Hiralal et al. [94] used reduced

graphene oxide (rGO) owing to its high surface area, mitigated the shape change of zinc anode with a reduction in dendritic growth, resulting in improved cycle life of 30 cycles instead of 4 cycles.

3.2.2. Nickel-cadmium (Ni-Cd) chemistry

Ni-Cd chemistry is well-established in popularity and maturity and has been successfully employed in various space orbital missions. Explorer 6 (1959) is known to be the first spacecraft utilizing a Ni-Cd battery, followed by TIROS, a weather satellite, various LEO missions (LANDSAT, TOPEX), GEO missions, and initial Mars orbital missions (MO, Magellan). These batteries can be utilized for operations where mass and volume are not crucial. This technology is preferred when the expected duration of the mission is 2–3 years long. These batteries are known to have 30,000 LEO cycles at 20–30 % DOD and exceeding 1000 GEO cycles at 50 % DOD [91].

In space missions, the power to weight ratio is significant as it incurs a high cost. Ni-Cd chemistry has a low energy density of 50–75 Wh/kg [95]. Although, Ni-Cd are known for their long cycle life, reliability, and low maintenance, they are still inadequate for the LEO orbiters, as it requires ~10+ years of operation with ~80,000 cycles. The outside satellite temperature could be as high as -180 to 200 °C, but these perform poorly in low temperatures (<-10 °C). Thus, the major constraint for extensive usage is their heavyweight (low specific energy and density), limited operating temperature range (-10 to 25 °C), and exhibition of memory-effect i.e., capacity fading when cycled at low DOD [96]. The failure of the Ni-Cd system is primarily because of the internal short circuits, deterioration of the separator, and electrolyte loss during prolonged cycling. Despite having good technical aspects, Ni-Cd chemistry does not emerge as a commercial success because of the high cost involved (\$ 1000/kWh, which is approximately ten times the lead-acid batteries) [95]. The other concern is the chemical constituents themselves- Cadmium is remarked as heavy toxic metal, while nickel and its corresponding oxides are categorized as carcinogenic under inhalation. The Ni-Cd system is known to have a high self-discharge rate because it has a negative temperature coefficient. It implies with increasing temperature; internal resistance falls to notable limits. Also, these Ni-Cd batteries employ aqueous electrolytes limiting the cell potential of 1.2 V thus, requiring a series of cells to acquire the desired voltage resulting in weight increment [97].

3.2.3. Nickel-hydrogen (Ni-H₂) chemistry

Nickel-hydrogen chemistry is widely employed in space applications where the crucial requirement is service life while mass and volume requirements are not the constraints. Among the available battery chemistry, especially for aerospace applications, Ni-H₂ chemistry is second to none regarding cycle life with decades of constant operation.

Ni—H₂ system has exhibited a surpassing cycle life (>50,000 cycles at 30 % DOD) and a long calendar life (>15 years of GEO operation) when compared to other available systems [91]. An excellent example of the Ni—H₂ is the Hubble-space technology, known to be operated for >15 years with limited battery deterioration [98]. The performance issues with the Ni—Cd chemistry-based spacecraft pushed the Ni—H₂ system into existence. Ni—H₂ and Ni—Cd weigh almost the same for the same capacity; however, the former provides higher cycle life for the same DOD; therefore, Ni—H₂ chemistry has a weight advantage over Ni—Cd chemistry in LEO oriented applications. Ni—H₂ chemistry is known to be the best fit for high-power GEO applications and has replaced Ni—Cd chemistry in most of the GEO applications where power requirement is >1 kW.

Ni—H₂ system is encapsulated in a pressurized vessel, where NiOOH is the active cathode material, while the anode is the hydrogen gas in a compressed state with aqueous alkaline KOH as the electrolyte. The concentration of KOH electrolyte varies depending on the oriented application 26–31 % for LEO and 31–38 % for GEO. Alike, fuel cells, a Teflon-bonded platinum black catalyst (supported on a photoetched nickel substrate) is employed to get the hydrogen gas into the solution.

The theoretical operating voltage of the cell is 1.25 V with low specific energy 40–75 Wh/kg with operational over a temperature range of –20 to 54 °C [99]. However, it has lost the whip hand over others due to its heavy weight, as weight is the driving parameter for cost estimation of the space mission. Also, the positive electrode is prone to swelling (corrosion), which results in high-rate self-discharge. These systems are not suitable for operations at low temperatures, as the electrolyte freezes below –25 °C, while wide operating temperature (low-temperature operation) is required for the LEO/GEO mission. The other concern is the possibility of hydrogen gas leakage and its flammability. The significant challenge with Ni—H₂ chemistry is the reduction of weight, volume, and cost. Developing a lightweight nickel electrode using design modification and fibrous substrate use could be an option. Replacement of individual pressure vessels with common pressure vessels with individual cells connected in series is yet another viable option. It has the advantage of reduced weight and cost involved. Similar to this, initiating a bipolar Ni—H₂ system is another strategy [100]. This bipolar system comprises individual unit cells electrically connected in series using conducting plates. This strategy has the advantage of reduced volume and high pulse power capability. In any conventional Ni—H₂ system, the usage of Pt catalyst adds to its cost, weight being the other parameter. In a recent study, Chen et al. demonstrated Ni—H₂ battery chemistry, which involves Ni(OH)₂ cathode and nickel-molybdenum-cobalt catalysed anode (bifunctional electrocatalyst for HER/HOR). This cell exhibits an energy density of 140 Wh/kg with insignificant capacity decay over 1500 cycles. The modified Ni—H₂ chemistry demonstrates great potential in extensive grid application with energy costing <\$100 kW/h [101].

3.3. Lithium-ion battery for space application

Li-ion batteries (LIBs) are presently being used for these missions because they are compact, lightweight (50 % weight reduction can be possible over Ni—H₂), and have much lower thermal dissipation. Also, LIBs have matured technology and are used in many consumer products. The current technological development of Li-ion batteries in their different electrodes and electrolyte systems can fulfil all the complex requirements of different space applications, as discussed in the section below.

3.3.1. High energy density batteries

For space exploration, it is critical to equip these spacecrafts with high energy density batteries, given the limitations in launch payloads with mass and volume. However, the performance factors of LIBs largely depend on the electrode chemistry employed. A conventional LIB employs graphite as an anode and a range of lithium metal oxides as a

cathode, where the Li-ion intercalates in the host structures that constitute a practical energy density of 150–200 Wh/kg. With the above chemistries of electrodes, the energy density of LIB is limited, resulting in an increase in the load and occupying a lot of space in spacecraft with high energy density battery requirements. A lot of advances have been accomplished in both electrode materials and Li-ion storage aspects to increase the energy density of LIBs. In 1991, Sony introduced the commercial LIB with layered oxides LiCoO₂ as an active cathode material, but it has a limited reversible capacity of 140 mAh/g. However, the capacity of these layered oxides cathode significantly increased by partially substituting Co with other metal ions such as Ni, Mn, Al, etc. Especially, Nickel (Ni)-rich lithium transition metal oxides (e.g., LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA), LiNi_{1-x-y}Mn_xCo_yO₂ (x + y < 1) (NMC)) with layered structure and having reversible capacities >200 mAh/g show great promise to improve the energy density in Li-ion cells. However, the energy density of these layered oxides cathode is limited due to their intercalation mechanism. Contrarily, few other metal oxides, nitride, sulfide, or halide compounds shows higher capacity due to their conversion reactions with Li⁺ [102], for example, Fan, X. et al. [103] developed a high-performance Fe_{0.9}Co_{0.1}O fluorinated cathode with a high capacity of ~360 mAh/g for 1000 cycles with a decay rate of 0.03 % per cycle.

In the case of the anode, the use of hard carbon as anode material has the advantages of high reversible electrode capacity and large operational voltage windows that have high storage capacity and demonstrate achieving high energy density LIBs. To realize much higher energy densities, the Si, Sn, and Ge-based anodes have been suggested for LIBs with practical achievable specific capacities >1000 mAh/g. However, the huge volume expansion during cycling leads to the pulverization of electrodes and capacity fading, which is detrimental to the battery performance. Careful design of such anode materials can address the above issues, e.g., many groups have reported Si nanowires use, self-healing conductive polymers, and porous structure resembling pomegranate. Liu et al. [104] reported that the volume expansion, low volumetric capacity, and detrimental side reaction of Si anode could be substantially reduced by a pomegranate-inspired architecture of nanostructured anode. Such anodes could not only be coupled with traditional LIBs but Li-air/O₂ and Li—S technology to realize high energy density batteries, as discussed in the section below. Furthermore, LIBs with conventional carbonate-based organic electrolytes involve safety issues when operated at elevated temperatures. During a thermal runaway condition, these electrolytes tend to decompose with increasing temperature and form O₂/CO₂ gas, causing the battery to expand, and a worst-case scenario could lead to an explosion. High energy density with relatively safer operation could be realized by using solid electrolytes in all-solid-state batteries (SSBs), as discussed in the below section.

3.3.2. Flexible battery

Future extravehicular activity (EVA) demands considerably more time and effort. EVA operations also integrate human crew with robots to explore the planetary surface at a faster rate than rover missions [105]. EVA operations need revolutionary energy generation and storage systems with different design and material integration systems. Current spacesuit designs in extended extravehicular activity (EVA) use heavy life support systems with limited power, which increases the mass and lowers the volume efficiency of the energy storage materials; therefore, they are not suitable for missions with significant gravitational fields with long time operation mission [106]. However, flexible batteries are a promising way to achieve high volumetric energy density compared to conventional approaches. In the flexible batteries, the active electrode material is directly coated on the surfaces of devices which gives the higher surface area of active material compared to the equivalent in conventional battery designs, where multiple layers of components are stacked together and sealed tightly inside of a container [107]. This rechargeable flexible battery is based on a solid-state

technology which can provide [108]: (i) adaptability to irregular geometric surfaces, such as the human body structure (ii) more number of operational cycles at 100 % depth of discharge (>10,000) (iii) high rate of charge or discharge nearly in 10 min (iv) improved safety by eliminating conventional liquid electrolytes (v) flexible, foldable, lightweight, and stretchable designs that allow the battery to be fabricated on/in spacesuit materials or components or device, (vi) The high surface area to volume packing efficiency, and (vii) support long-duration mission by reducing parasitic mass and volume. Significant advancement has been made in flexible LIBs for developing flexible solid electrolytes, implantable electrode materials, new structural designs, and suitable fabrication methods.

The flexible lithium-ion battery also has a similar structural design to conventional LIBs. However, a flexible LIB needs a flexible electrode with low self-discharge, high capacity, stable cycling performance, and high-rate capability. Also, polymer or solid-state electrolytes with high ionic conductivity, excellent mechanical flexibility, and high electrochemical, thermal, and mechanical stability [108]. In conventional battery design, the electrode is prepared by the coating of active electrode material slurry on the top of a conductive metal foil current collector (e.g., Cu and Al). However, these electrode materials peel out from the substrate when it undergoes mechanical deformation such as bending or folding. Hence, to prepare a flexible electrode conventionally is not suitable. Therefore, we need different strategies to prepare substrate, active materials, and electrolytes to develop flexible LIBs. Following are the strategies widely used to prepare the flexible electrode [109,110]:

(i) Use of conductive flexible carbon-based material as substrates:

Carbon material, such as carbon nanofibers, graphene, carbon cloth, carbon nanotubes, and carbon papers, is widely used as self-supporting flexible electrodes instead of metal current collectors due to its high electrical conductivity, high flexibility, thermal and chemical stability, mechanical properties, and exceptional surface properties.

(ii) Use of flexible polymers, non-conductive substrates, nanostructured active materials, and others

Polymers are used in electrodes to achieve high flexibility for example, sulfur-linked carbonyl-based poly (2,5-dihydroxyl-1,4-benzoquinonyl sulfide) (PDHBQS) and 3,4,9,10-perylenetetracarboxylic diimide (PDI) [110]. The nonconductive substrates are also flexible, mechanically robust, and porous and used as flexible electrodes to obtain high-performance flexible batteries. The nonconductive substrates include commonly used separators (Celgard 3500), PDMS, poly (*m*-phenylene isophthalamide), textiles, cotton, cloth, cellulose paper, and other polymers [109]. Except from the CNTs, graphene, and other carbon-based material, nanostructured active materials are also used in flexible LIBs due to their high aspect ratio and short ion/electron transport distance. These flexible nanostructured materials include 2D assembly of Co₃O₄ NWs with a conductive Au coating, Si-NW fabric coated with the conductive carbon layer, and Porous Li₄Ti₅O₁₂ nano-sheets with an N-doped carbon coating [111]. MXene is a 2D material used in flexible batteries due to its high surface area, superior electrical conductivity, lightweight, flexible, low lithium-ion diffusion barrier, and good mechanical properties [112,113].

The flexible cathode materials such as LiCoO₂, LiMn₂O₄, LiFePO₄, and V_xO_y, are prepared by incorporating various flexible conducting substrates such as CNTs, graphene, carbon nanofibers, ultrathin graphite foam, carbon cloth, etc. [114]. Currently, liquid organic electrolytes offer significant advantages of high conductivity, compatibility with anode, and cathode with long cycle performance. However, the use of liquid electrolytes in flexible batteries has a considerable safety concern because of their limited thermal and electrochemical stability and mechanical robustness. Therefore, most flexible LIBs preferred polymer-

based electrolytes for their higher safety, mechanical compliance, thermal stability, and technical readiness [115,116]. The polymer electrolytes can be broadly divided into three large categories as gel polymer electrolyte (GPE) containing solvent, solid-state polymer electrolyte (SPE), and composite polymer electrolyte (CPE) with or without solvent [117]. In case of GPE, polyimide, poly(ethyl cyanoacrylate), poly(vinylidene fluoride) (PVDF), poly(arylene ether), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) have been extensively investigated [115]. Typical polymers used for SPEs, include polyethylene oxide (PEO), polycarbonate, and polysiloxane [116]. To overcome the low ionic conductivity at room temperature and high contact resistance of SPE, CPEs composed of SPEs and inorganic nanoparticles/additives have been investigated [78], which include Al₂O₃, TiO₂, Li_{1+x}Al_xGe_{2-x}(PO₄)₃, perovskite Li_{0.33}La_{0.557}TiO₃, garnet Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂, Li₁₀GeP₂S₁₂, Li_{6.28}La₃Zr₂Al_{0.24}O₁₂, etc. [99].

3.3.3. High-temperature battery

The outer missions (such as Venus and Mercury) require battery technology, to operate at high temperatures. However, conventional commercial lithium-ion batteries mostly operate in the temperature range of -25 °C to 60 °C but their maximum survivable temperature of ~80 °C. Therefore, it's not suitable for outer planetary missions. Beyond this operating temperature, the cell undergoes loss of lithium, reduction of active materials, irreversible electrode/electrolyte reaction, irreparable damage, increasing internal resistance, reduced cell capacity, loss of power, reduced cell lifetime, and in some cases, cell catches fire, or it explodes [118]. Currently, researchers are making lots of effort to extend the operating temperature of lithium-ion secondary batteries by developing a cathode, anode, electrolyte, and a stable interface between the electrode and the electrolyte. Cathode oxide materials such as NMC, LNMO, and LCO are utilized in the current lithium-ion battery; however, they are unstable at elevated temperatures, can reduce exothermic disproportionation reactions, and produce gases such as O₂, CO₂, and CO. For example, the thermal breakdown of lithium cobalt oxide (LCO) during charge can release oxygen, as shown in the following equation [119].



The thermal stability of layered oxide materials is low such as LCO having 150 °C [119]. It has been observed that below 300 °C, these materials decompose and release O₂ because of the high effective oxygen partial pressure, which can further react with an organic solvent, leading to a thermal runaway phenomenon [120]. However, the LiFePO₄ and other olivine structures have excellent safety, high-rate capability, and long-term cycle and are stable up to at least 400 °C and demonstrate the potential to be utilized as cathodes for inner planetary space missions [121]. The layered structure cathode and LiFePO₄ comparison reported at 55–60 °C shows the high performance of the latter due to structural stability (oxygen atoms are covalently bonded to phosphorous in PO₄ units instead of transition metals M) and chemical stability (having Fe^{2+/3+} rather than M^{3+/4+} in LiMO₂ materials) [122].

The LiFePO₄/artificial graphite (AG) electrode configuration was investigated with lithium oxalyldifluoroborate (LiODFB) based organic electrolyte and showed excellent capacity retention of ~88 % after 100 cycles, much higher than that of LiPF₆-based electrolyte at 65 °C [124]. Further performance of the LFP cathode increased with polymer electrolyte, ionic liquid, and solid-state electrolyte. Qichao Hu et al. [124] reported the temperature stability and cycling behavior of LiFePO₄ cathode in lithium battery with graft copolymer electrolyte (GCE). This copolymer electrolyte consists of poly(oxyethylene) methacrylate-g-poly (dimethylsiloxane) (POEM-g-PDMS) doped with lithium triflate. This GCE-based cell was tested for charge and discharge cycling at temperatures of 120 °C. David Muñoz-Rojas et al. [125] designed and tested LiFePO₄ as a cathode with LiTFSI as a molten salt electrolyte and

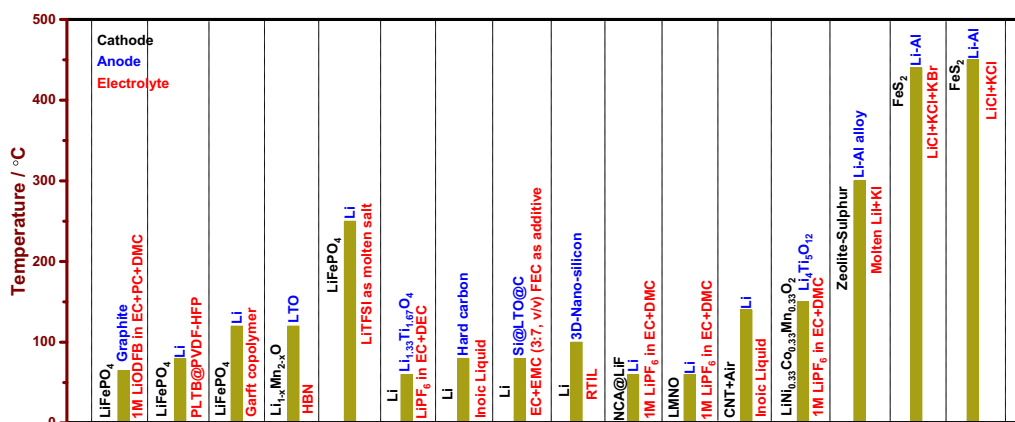


Fig. 4. Lithium-ion battery development with a respective high-temperature operating conditions; data collected from ref. [125–140].

metallic lithium as an anode at 250 °C.

Yiqing Huang et al. [121] showed the higher thermal stability of other multielectron vanadyl phosphates, such as VOPO₄, LiVOPO₄, and Li₂VOPO₄. It has been observed that VOPO₄ reacts with the electrolyte between 200 °C and 300 °C, but it does not have the O₂ evolution issue as layered oxide materials making it inherently safe and showing promise to be utilized in inner planetary space missions. Furthermore, the thermal stability of layered-based cathode can be increased by elemental doping and surface coating such as F-doped LiMn_{1.5}Ni_{0.5}O_{4-δ} (LMNO) [123] and (LiF)-coated NCA [126].

Fig. 4 shows the development of lithium-ion batteries with respective high-temperature operating conditions. A battery system with Li–Al anode, FeS₂, and salts of metal halides as electrolyte show much promise and satisfactory performance at elevated temperatures of 450 °C which could be utilized for inner planet (Mercury and Venus) missions. Nevertheless, significant developments are still expected to be made to ensure the proper operation of these battery systems. The thermal stability and electrochemical stability of lithium-ion cells can be achieved by the use of ionic liquid (IL) and hybrid IL/organic electrolytes. It has been observed that pyrrolidinium cation-based ILs have high thermal stabilities (340 °C), ionic conductivities of $>5 \times 10^{-3} \text{ S cm}^{-1}$ at 80 °C, and broad electrochemical stability windows: 0–5 V vs. Li⁺/Li^o [141]. Manfred Kerner et al. [142] investigated ternary lithium-salt/ionic liquids (IL)/polymerized ionic liquids (PIL) electrolytes for high-temperature lithium-ion batteries (HT-LIBs). These electrolytes are thermally stable at ≥ 100 °C, and with TFSI anion, the electrolytes have higher thermal stabilities at ≥ 125 °C.

As conventional LIB uses flammable organic liquid electrolytes that have a risk of boiling, freezing, or burning at high-temperature operation. And thus, needs to be replaced, expanding the thermal stability of the LIB. However, all-solid-state type LIBs consisting of the cathode, solid electrolyte, and anode material is an expected promising technology for next-generation energy storage devices because of their safety, reliability, high energy density, and incombustibility over the conventional electrolyte and separate system [126,127].

However, solid electrolytes (e.g., LiPON) show significantly lower room-temperature ionic conductivities of $\sim 10^{-6} \text{ S cm}^{-1}$ compared to liquid electrolytes LiPF₆ in EC-PC ($10^{-2} \text{ S cm}^{-1}$). It limits the overall operational performance of lithium-ion batteries at room temperature [143]. The operation of these solid-state batteries at higher temperatures can overcome the problem associated with it at room temperature, such as lithium-ion conductivity and reduction in the interfacial electrode-electrolyte resistance. However, the solid electrolyte such as LiPON and LiGeP₂S₁₂ (LGPS) show excellent ionic conductivities over the conventional liquid electrolyte at elevated temperatures; for example, Li₁₄Zn(GeO₄)₄ (LISICON) shows ionic conductivity of $\sim 10^{-1} \text{ S cm}^{-1}$ at 300 °C compared to liquid electrolytes LiPF₆ in EC-PC at room temperature $10^{-2} \text{ S cm}^{-1}$ [144].

3.3.4. Low-temperature battery

Low-temperature batteries are essential for space exploration of an extremely cold planet such as Mars, with an average temperature of approximately –60 °C. However, the operation of these batteries at low temperatures leads to low electrolyte conductivity, electrode

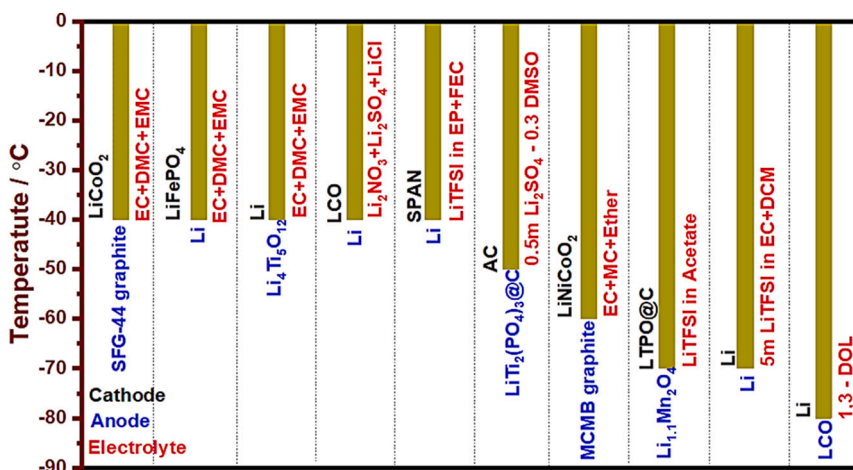


Fig. 5. Lithium-ion battery development with respective low temperature operating conditions; data collected from ref. [147–156].

passivation, low Li^+ diffusion, and slow kinetics, and requires thermal management. Therefore, developing batteries with the inherent ability to operate at low temperatures with a minimum thermal management requirement is a challenging task for space applications. Academic and industrial researchers have been working on improving the low-temperature performance of the lithium-ion battery by altering the property of electrolyte, electrode, co-salt, and solvent and the use of additives. The low-temperature performance of lithium-ion cells is studied with different ratios of alkyl carbonate solvent mixtures, i.e., ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC). It has been observed (Fig. 5) that electrolytes based on the ternary mixtures of EC, DEC, and DMC emerged as the preferred combination at a low-temperature performance of Li-ion cell compared to the binary mixture of conventional electrolytes in terms of electrolyte conductivity, film resistance, film stability, and kinetics of lithium intercalation and de-intercalation [145]. The developed ternary mixtures of EC, DEC, and DMC (1:1:1 v/v) and 1.0 M LiPF_6 electrolyte configured with the MCMB- LiNiCoO_2 electrode in the lithium-ion cell has been utilized for Mars Exploration Rover (2003), Phoenix Mars Polar Lander, and other missions [146]. Fig. 5 shows the development of low-temperature LIB that could be utilized in space missions for the cold planet. Various electrode systems (anode and cathode) are utilized to examine their efficacy at low-temperature conditions employing various electrolyte systems.

LiFePO_4 cathode performance at low temperatures with a ternary mixture of EC, DEC, and DMC (1:1:3, vol%) was reported by charge/discharge test and electrochemical impedance spectroscopy (EIS) [150]. The electrochemical performances of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -rutile TiO_2 (LTO-RTO) composite electrodes were also evaluated at low temperatures with a ternary mixture of EC, DEC, and DMC electrolyte [149]. To improve the performance of lithium-ion cells at low temperatures (i.e., -60°C), the addition of low-viscosity esters co-solvents such as methyl acetate, ethyl acetate, γ -butyrolactone, and ethyl methyl carbonate with ethylene carbonate-based electrolytes has been investigated. The cells with the 0.75 M LiPF_6 , EC + DEC + DMC + MA (1:1:1:1) and 0.75 M LiPF_6 , EC + DEC + DMC + EA (1:1:1:1) electrolytes showed superior performance at -40°C [146,158]. Further, quaternary carbonate-based electrolytes systems (i.e., 1.0 M LiPF_6 EC + DEC + DMC + EMC (1:1:1:3 v/v)) have been reported to improve the low temperature (at -40°C) performance of lithium-ion cell with MCMB-carbon anode, and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode [157]. The aqueous electrolytes based on three low-cost inorganic salts (LiNO_3 , Li_2SO_4 , and LiCl) show excellent performance of lithium-ion batteries at very low temperatures of -40°C [158]. Dimethyl sulfoxide (DMSO) as an additive with a molar fraction of 0.3 to an aqueous solution of 2M NaClO_4 (0.3-2 M) electrolyte is configured with activated carbon anode and $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ cathode shows the lithium-ion cell is operating very well even at -50°C [159]. An ethyl acetate (EA)-based electrolyte (i.e., the solvent of EA and lithium bis (trifluoromethane sulfonyl) imide (LiTFSI), salt) is developed to resolve the sluggish de-solvation of Li^+ at the low-temperature operation of the battery. The (EA)-based electrolyte with spinel $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ (LMO) anode and carbon-coated NASICON-type $\text{LiTi}_2(\text{PO}_4)_3$ (LTPO@C, as cathode material tested in Lithium-ion cell and work well at an ultra-low temperature of -70°C [153]. Adding dichloromethane (DCM) as a diluent in concentrated ethyl acetate (EA)-based electrolyte improved the ionic conductivity and low viscosity. This addition of DCM in EA electrolytes improved the further performance of lithium batteries at -70°C in terms of energy and power density [160]. Further, the low-temperature operation of a Li-ion battery can be extended to -80°C by utilizing a 1,3-dioxolane-based electrolyte with LTO anode material which displays its potential to be utilized in Mars space missions [151]. The advanced Li-Sulfur battery also showed better performance at low-temperature operation; for example, the mixed solvents 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME), and tetraethylene glycol dimethyl ether (TEGDME) with an equal ratio of DOL: DME: TEGDME (1:1:1 by volume) developed for lithium-sulfur

battery and work well at a low temperature of -40°C [161]. Also, a novel lithium bis(fluorosulfonyl)imide in methyl propionate/fluoroethylene carbonate (LiFSI MP/FEC) electrolyte system was designed for lithium-sulfur battery with sulfurized polyacrylonitrile (SPAN) cathode, which can be operated at a low temperature of -40°C [147].

3.3.5. Solid-state battery

Solid-state batteries (SSB) attained enormous attention over conventional batteries due to their high energy density and safer operation during usage. Aerospace application batteries need to sustain in extreme temperature conditions available widely in space [162]. The feasibility of these batteries has to be explored in extreme conditions (high and low temperature and pressure under an inert atmosphere). The main component that needs to be designed for a stable performance SSB is electrolytes which work efficiently at the lower and higher temperature without hampering the properties of the electrolyte, such as decomposition temperature, ionic conductivity, etc. [163,164]. The scientific community dedicated tremendous efforts to synthesizing the appropriate electrolyte composition that can be effectively used for these applications. H. Song and his team [162] have proposed the feasibility of solar-driven all-solid-state lithium-air batteries at ultra-low temperature (-73°C) using plasmon-enhanced solar photothermal technology. The components used in this study are lithium metal as an anode, plasmonic air as a cathode, and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ (LAGP) as a solid-state electrolyte. Furthermore, to ensure efficient light adsorption, single-layer plasmonic Ru nanostructures were assembled on the cathode. The as-prepared battery assembly delivered an extremely high reversible capacity of 3600 mAh/g (under Xe-lamp irradiation) at -73°C with a current rate of 400 mA/g with excellent cycle life at -73°C and room temperature. Michael et al. [165] developed a solid-state battery with a "Li-free" cell configuration with NCA/PEO-composite cathode, LLZO, and in situ-plated Li-metal anode, which can be operated at 60°C . In another study, Hirokazu et al. [166] showed the feasibility of a lithium-oxygen battery that can be operated at elevated temperatures of 80°C & 120°C by the exploration of solid electrolyte $\text{Li}_{1.575}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$. The battery performance was evaluated from room temperature to 120°C . The cell delivered a reversible capacity of 1420 mAh/g at 10 mA/g, evaluated at room temperature. The cyclic stability was performed at room temperatures, 80°C and 120°C , with a capacity limit of 500 mAh/g. The cell demonstrated high-capacity retention after 20 cycles, and the coulombic efficiency was 90–98 % showing the feasibility of reversible reaction. Furthermore, another investigation by Zehua et al. [167] shed light on the feasibility of all-solid-state lithium-ion batteries. In this work, they have developed solid electrolytes by cross-linking starch and investigated their performance below room temperature (0 & -20°C). The battery delivered an initial reversible capacity of 85 mAh/g, maintaining an average capacity of 114 mAh g^{-1} during 200 cycles at 0°C and 0.1C. In addition, the measurement carried out at -20°C revealed an initial reversible capacity of 47.5 mAh/g with an average capacity of 60 mAh/g even after 300 cycles at 0.1C. The performance was also evaluated at various temperatures (25°C & 45°C) and revealed excellent electrochemical behavior, ascribed to the efficient working of the as-prepared starch cross-linked electrolyte that enables the reaction at various temperatures. Another study on high temperature by Seok H. Lee et al. [168] showed the feasibility of an all-solid-state lithium-ion battery utilizing solid electrolyte ($\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$) and $32\text{LiCoO}_2/65\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}/3\text{MWCNTs}$ as an electrode-electrolyte-electrode assembly. The performance of the as-prepared assembly was investigated at the temperature of 120°C with current rates of 0.036C to 0.18C. A thorough investigation at temperatures of 80°C and 120°C revealed an excellent rate of performance at 120°C as compared to 80°C . The increment in electrochemical performance can be associated with better kinetics and ionic conductivity at elevated temperatures. The work by W. Xiao et al. [169] presented another study for SSB battery enabled with $\text{Li}_{6.25}\text{PS}_{5.25}\text{Cl}_{0.75}$ as a fast ion-conductive electrolyte at 60°C . They prepared $\text{LiCoO}_2/\text{LiNbO}_3$ (cathode)/ $\text{Li}_{6.25}\text{PS}_{5.25}\text{Cl}_{0.75}$

Table 6

List of solid-state lithium-ion batteries at extreme temperature conditions [162,166–169].

Cell configuration (Cathode/ Electrolyte/Anode)	Temperature (°C)	Electrochemical performance
Plasmonic air/ Li _{1.5} Al _{0.5} Ge _{1.5} P ₃ O ₁₂ / Lithium	–73	Cycle life – 50 @ 400 mA/g Capacity limit – 1000 mAh/g
Li/Li _{1.575} Al _{0.5} Ge _{1.5} (PO ₄) ₃ / LAGP-carbon nanotube (CNT)	80, 120	Cycle life – 10 @ 10 mA/g Capacity limit – 500 mAh/g
32LiCoO ₂ /65Li ₅ La ₃ Ta ₂ O ₁₂ / 3MWCNTs	120	Capacity retention – 80 % after cycling at higher current rate (0.36C to 0.036C)
LiFePO ₄ (LFP)/BStSi/Li	0, 20	Capacity retention – 100 % after cycling at higher current rate (0.3C to 0.1C)
LCO@LNO/Li _{6.25} PS _{5.25} Cl _{0.75} / Li	60	Capacity retention - 74.12 % after 430 cycles at 100 μ A/cm ² 59.7 % of capacity after 800 cycles at 50 μ A/cm

(electrolyte)/Li (anode) assembly and displayed an excellent capacity retention of 74.12 % after 430 cycles at 100 μ A/cm² while 59.7 % after 800 cycles at 50 μ A/cm². The excellent electrochemical performance can be associated with superb ionic conductivity of the electrolyte rivalling the current liquid electrolyte. The summary of different electrode-electrolyte used for extreme temperature conditions is summarized in Table 6.

Based on the above discussion and findings, this study paves a wide direction to investigate the stoichiometric mismatch compounds of lithium as a promising cathode material. Moreover, the feasibility of the devices investigated at various extreme temperature provide insight for further rigorous analysis in the field for a solid electrolyte for safer operation of devices. As space applications involve extreme conditions, the all-solid-state battery is one of the most appealing candidates. However, the challenges of the solid-state battery need to address to enable it for space application. Special attention must be devoted to the optimization of solid-state electrolytes that offers ionic conductivity equivalent to liquid electrolytes without the usage of flammable liquid solvents. As in solid-state batteries, the stacks are prepared by applying pressure using layers of the electrode (cathode)/electrolyte/electrode (anode) assemblies. The applied pressure during the fabrication of the composite should be large enough so that there would not be detachment from the current collector. Moreover, for the space application, the feasibility of the operation at extreme (low and high) temperatures should also be investigated rigorously.

3.3.6. Beyond lithium-ion battery

The present developed LIBs have limited energy density due to their intercalation chemistry which can limit LIBs use in the high energy density requirement of planetary and space missions, such as Astronaut's Portable Life Support System (PLSS) for ExtraVehicular Activities (EVA), small planetary rovers, planetary probes, CubeSats, etc. [170]. Lithium-sulfur (Li–S) batteries present a promising solution over conventional lithium-ion batteries due to the high theoretical specific capacity (1675mAh/g) and specific energy density (2500Wh/kg) of sulfur cathode [171]. In Li–S batteries, the sulfur cathode is used, which is one of the most abundant elements on the Earth, is environment friendly, and has a low cost. However, there are many challenges to the commercialization of Li–S batteries, such as [172–175] (i) dissolution of higher-order lithium polysulfide in an organic electrolyte and their shuttling in between two electrodes; (ii) poor electronic conductivity of sulfur cathode, which leads to sluggish kinetic process with poor utilization of active material; (iii) fracture or pulverization of active material due to the volume expansion in electrode and (iv) Li metal anode corrosive reactions with electrolytes and the growth of dendrites. This, in turn, leads to a loss of capacity, low columbic efficiency, and limited cycle life

of the battery. In the past decade, numerous efforts have been made to overcome the stumbling blocks of Li–S batteries. To resolve the polysulfide shuttling issue, Aurbach and co-workers investigated the lithium nitrate (LiNO₃) additive, the presence of LiNO₃ forms a protective layer on the lithium metal anode, which prevents a shuttle mechanism with an increase in the Coulombic efficiency to 98 % [176]. Further, to tackle the poor electronic conductivity of sulfur cathode, Xiulei Ji et al. [177] proposed a melt-diffusion method to incorporate sulfur within conductive carbon materials that significantly resolved the insulating nature of sulfur. Porous carbon matrices such as mesoporous and microporous carbon have been utilized to mitigate the volume change and sulfur utilization issue [178]. However, the lithium anode issues can be tackled by the electrolyte regulation, artificial coating, and pre-treatment of electrodes [179].

Currently, only a few companies are producing commercial Li–S cells, such as Sion Power in the US and OXIS Energy Ltd. in Europe [180]. Bruno Samaniego et al. [181] tested these commercial Lithium-Sulfur cells for space applications, particularly for LEO, GEO, and launcher applications. It was observed that Li–S battery technology shows great potential for launchers or satellite missions due to its high energy density; however, the performances regarding cycling, rate capability, and temperature need to be further improved.

Lithium batteries (Li-ion/Li-S) are small in size, lightweight, and durable over other commercial batteries. However, the lithium-air system is the most viable “Metal-air” technology because of its high theoretical specific energy density over Li-ion and Li–S batteries. Thus, metal-air batteries (e.g., Li-air batteries) can contribute to a significant enhancement of several planetary and space missions where battery technologies require higher specific capacity and energy densities for a short lifetime. Currently, there are four types of Li-air batteries based on the use of electrolytes [182], namely i) a fully aprotic/non-aqueous liquid electrolyte, ii) an aqueous electrolyte, iii) a mixed/hybrid system, and iv) an all-solid-state battery using a solid electrolyte. High energy-density lithium-air battery also utilized in extremely low temperatures for space missions. H Song et al. [162] proposed solar photothermal aerospace-grade all-solid-state lithium-air batteries technology, which can operate at ultra-low temperatures. These batteries show promising electrochemical performance with a high discharge capacity of ~3600 mAh/g and long cycle life at –73 °C [162]. There are challenges for lithium-air batteries, such as the growth of lithium dendrites and the parasitic reaction of Li with H₂O/CO₂, limited oxygen solubility and slow kinetics of oxygen reactions, accumulation of reaction products at the cathode, over potential or polarization losses during discharge and charge, and degradation of carbon cathodes electrode [183].

Currently, Li-CO₂ has also attracted much attention due to its high theoretical specific energy density (1876 Wh/kg) with high discharge potential (~2.7 V) and efficient utilization of greenhouse CO₂ gas [184]. Furthermore, the researchers are exploring the lithium-carbon dioxide (Li-CO₂) battery energy-storage systems in extreme environments with ultra-high CO₂ concentrations for space missions, particularly on Mars, due to the presence of 96 % CO₂ in the atmosphere. Recently, our research group developed a prototypical rechargeable Li-CO₂-Mars battery operated in a simulated Martian atmosphere consisting of Carbon dioxide (95.32 %), Nitrogen (2.7 %), Argon (1.6 %), Oxygen (0.13 %), and Carbon Monoxide (0.08 %) [185]. Li-CO₂-Mars battery chemistry is mainly developed to explore the feasibility of this technology in the Mars mission, particularly for surface landers and rovers, which significantly can reduce the mass, volume, and overall cost of space missions [185].

The feasibility of a Li-CO₂ battery with 96 % CO₂ at atmospheric conditions is mostly explored. Still, it is also vital to investigate the battery performance at a lower temperature because Mars is a cold planet with an average temperature of approximately –62 °C. Jiixin Li et al. [186] designed 1,3-dioxolane-based electrolyte and iridium-based cathode for ultra-low-temperature Li-CO₂ batteries. This battery shows a

fixed discharge capacity of 500 mAh/g for a long lifespan of 150 cycles (1500 h) at $-60\text{ }^{\circ}\text{C}$. Further, the battery is tested at ultralow temperatures ($-70\text{ }^{\circ}\text{C}$) varied according to realistic temperature fluctuations over a period on Mars. However, the simultaneous influence of other Martian atmospheric parameters such as pressure and humidity needs to be investigated in detail.

Furthermore, to obtain the full potential of Li- CO_2 battery in a space application, we need to address the fundamental challenges of this battery chemistry, such as poor reversibility of Li metal and CO_2 chemistry, large overpotential during CO_2 reduction, CO_2 evolution reaction (CRR & CER), Li metal dendrite growth, capacity degradation, and low round-trip efficiency during long cycling.

Although lithium-based batteries are the most suitable and mature technology for space and large-scale applications, the continuous consumption of limited reserve lithium and cobalt has increased the cost of Li-ion battery by more than six times in the last decade. The lithium price is sensitive and subject to supply and demand considerations, whereas cobalt is in short supply due to reserves located in volatile regions. On the contrary, due to the abundance of sodium, the sodium-ion battery stands out as an alternative battery technology, providing both a low-cost and "cost-stable" energy storage option for large-scale energy storage applications. However, the sodium-ion battery is still in its early stage compared to robust, mature, and well-established Li-ion battery technology. Moreover, Na-ion batteries are relatively heavier (low energy density) than Li-ion batteries occupying larger space and volume in the spacecraft thereby increasing the overall cost of the mission [187,188]. Considering the low energy metrics and limited cycle life of

Na-ion batteries at extreme operating conditions are considered an obstacle in the practical application of Na-ion batteries for space applications.

Significant effort has recently been made for performance improvement of Na-ion batteries in extreme conditions (high and low temperature); for example, titanium-based anodes and polyanionic cathodes with organic carbonate electrolytes will be a good choice for Na-ion batteries at low-temperature conditions. Whereas the development and utilization of solid electrolytes (e.g., glass-ceramic electrolytes) will be the way forward for high-temperature operation development. Further details about the current state of art development of Na-ion batteries including critical challenges for high and low-temperature conditions can be found in other reports [188,189]. Nonetheless, widespread commercialization and mass production of Na-ion battery is still dependent on further development, optimization, and market acceptance, including considerations for electrode and cell design to improve energy density and battery pack integration.

3.4. Supercapacitor

Secondary batteries-based energy storage systems are noteworthy for power space missions because of their high energy density and specific energy (Fig. 6a). However, this technology is limited regarding power density and performance at extreme pressure and temperature conditions prevailing in space. In the meantime, another class of energy storage system, the supercapacitors, particularly, electric double-layer capacitance (EDLCs), has gained acceptance in this regard. EDLCs

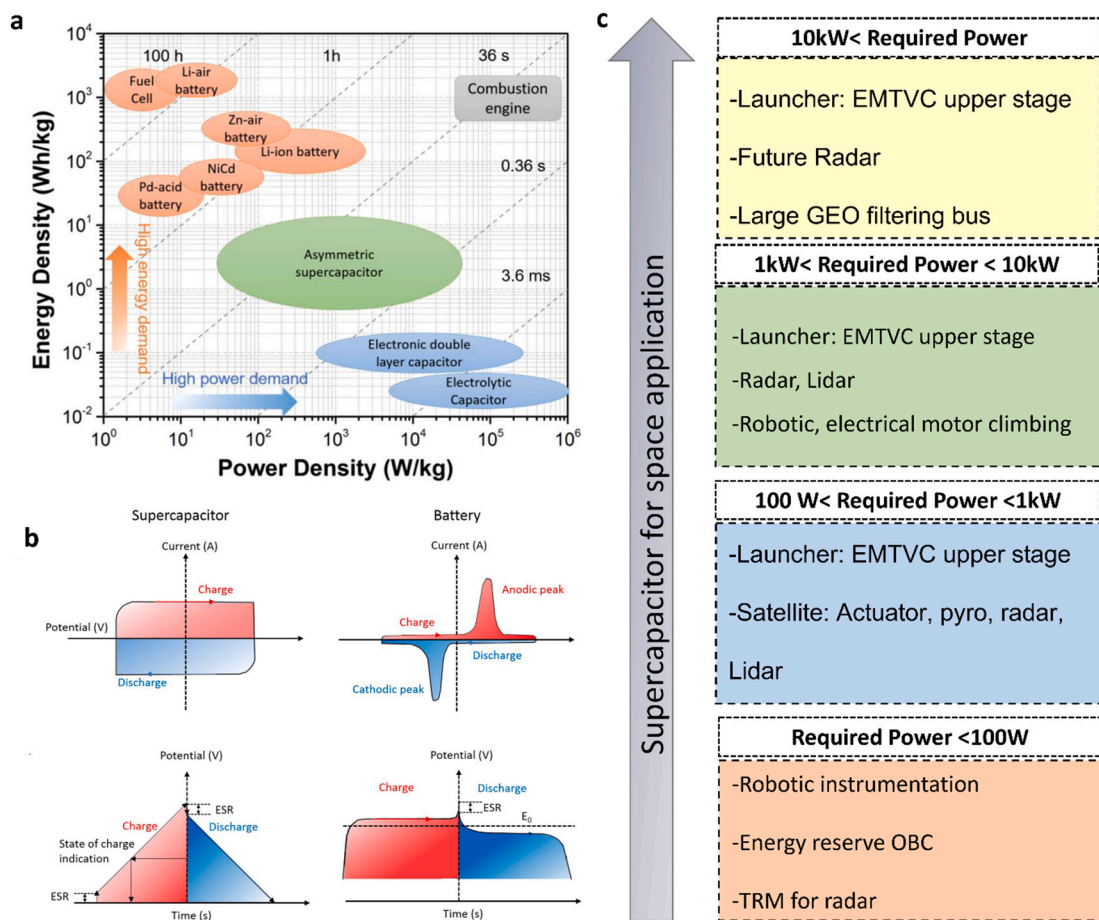


Fig. 6. a. Comparison of specific energy and specific power of supercapacitor over the other energy-storage technologies. b. Electrochemical behavior of supercapacitor and battery c. Potential application of supercapacitors for space application based on their power requirements. Reproduced with permission. [201] Copyright 2018, American Chemical Society.

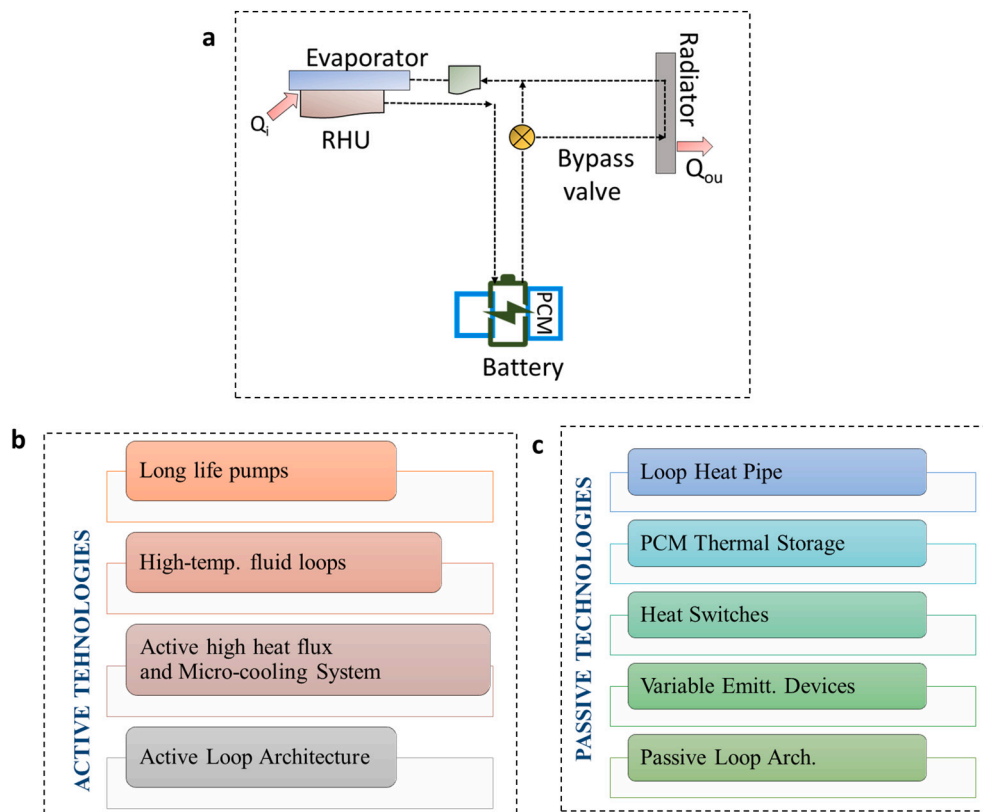


Fig. 7. a. Schematic of the thermal control unit for Mars lander and Rover batteries. b. Active thermal protection technologies, c. Passive thermal protection technologies.

energy storage mechanism utilizes the physical phenomena of ion adsorption at the electrode-electrolyte interface rather than a chemical reaction occurring in batteries (Fig. 6b). The absence of an electrochemical reaction dictates quick charge-discharge resulting in high power density compared to secondary batteries. This non-faradaic process renders long cycle life with reduced degradation of the involved material compared to battery materials. Additionally, these EDLCs are known to be operational for a wider range of temperatures than batteries. In short, EDLCs have some exceptional advantages over secondary batteries, particularly in terms of long life, high-power delivery, fast charge-discharge, and wide temperature range operation with minimal material degradation rendering them of interest for space-related applications. The use of EDLCs in space missions can be numerous, say regulation of power systems or pyrotechnic processes, or thrust actuators, given the capability of withstanding the extreme space environment. Extensive research efforts are going on to enhance the utility of EDLCs in harsh space environments.

The space application demands an operational range of very high temperatures as 400–450 °C and as low as –160 °C. The EDLCs technologies have an operating temperature range of –60 to +60 °C, but space applications demand more operating temperature range. Here, the temperature limitation is due to the material property, which is temperature-dependent; therefore, desirable performance at such a wide range of operating temperatures is extremely challenging. However, research attempts are continuously being made for EDLCs operating at high and low temperatures. The electrode material and the electrolyte are of prime importance when needed to realize thermal extremes operation. Despite struggling with efforts to alter the operational temperature range using microstructure modification of the electrode material, the achieved range was restricted to –20 to 50 °C for graphitic

carbon [190], –40 to 100 °C for activated carbon fabric, and –50 to 80 °C for onion-like carbon [191] respectively. However, an improved temperature range of –40 to 200 °C has been reported for rGO-based electrodes [192], while in another report, the temperature range has been further extended from –70 to 220 °C [193].

Electrolytes can be categorized as liquid (aqueous, organic, and ionic) and solid-state electrolytes (polymer or gel). Aqueous electrolytes are preferred owing to their conductivity and safety. However, at high temperatures, the aqueous electrolyte will decompose, whereas at a temperature lower than sub-zero aqueous medium freezes, and salt precipitation occurs, decreasing the ionic conductivity, thereby hampering the performance. There are reports of concentrated aqueous electrolytes which could be employed below 0 °C because of low freezing points [194,195]. Another approach could be the substitution of pure water with binary solvents with cryoprotectants [196]. Thus, aqueous electrolytes are fit for operation between –20 to 80 °C [197]. The organic electrolytes allow a higher operating potential window but suffer poor conductivity and have low boiling points disrupting desired performance at elevated temperatures. Instead, ionic liquid with higher thermal stability is more suitable for a wide range of operation temperatures [198]. The use of solid-state electrolytes can be used at low (<0 °C) and high temperature (100 °C) operations but has low conductivity when compared to liquid counterparts [193].

Lately, there are reports of on-ground investigations scrutinizing the possibility of terrestrial COTS (commercial off-the-shelf) supercapacitors for space applications. In one of the reports, the authors conducted life tests on COTS supercapacitors available in the market and evaluated their performance. This study enabled them to identify suitable areas for its usage [199]. Besides, on-ground investigations and an in-orbit demonstration of the COTS-supported payload of a satellite

Table 7
List of space reactor power systems [210].

	SNAP 10	SP-100	Romashka	Bouk	Topaz 1	Topaz 2	SAFE-400
Year	1965	1992	1967	1977	1987	1992	2007
kW _{th}	45.5	2000	40	~100	150	135	400
kW _e	0.65	100	0.8	~5	5–10	6	100
Transducer	TE	TE	TE	TE	TI	TI	TI
Fuel	U-ZrH _x	UN	UC ₂	U-Mo	UO ₂	UO ₂	UN
Mass-kg	435	5422	455	~390	320	1061	512
Neutron Spectrum	Thermal	Fast	Fast	Fast	Thermal	Thermal/Epithermal	Fast
Coolant	NaK	Li	None	NaK	NaK	NaK	Na
Core temp. °C	585	1377	1900	NA	1600	1900	1020

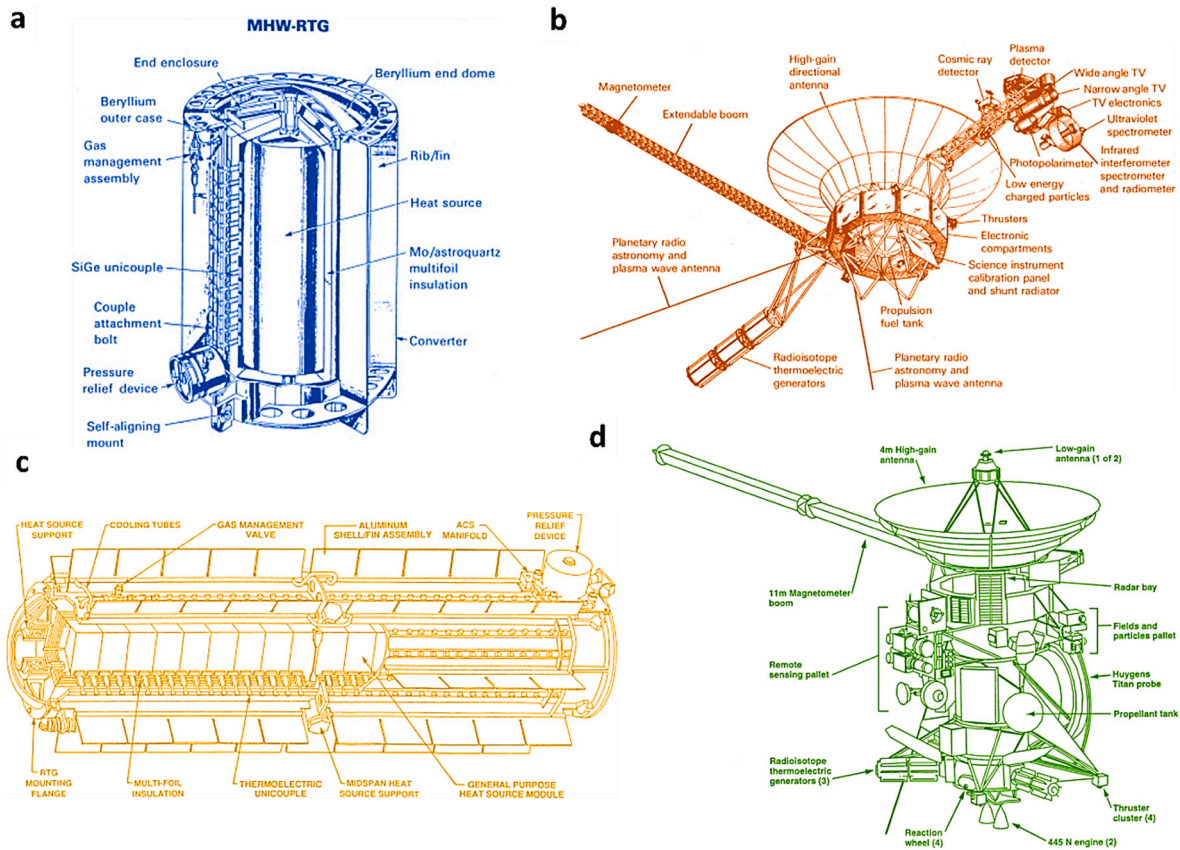


Fig. 8. a. Multi-Hundred-Watt Radioisotope Thermoelectric Generator (MHW-RTG). b. Use case of MHW-RTG in Voyager spacecraft. c. General-Purpose Heat Source Radioisotope Thermoelectric Generator (GPHS-RTG). d. Use case of GPHS-RTG on the Cassini spacecraft. Reproduced with permission. [207] Copyright 2003, Elsevier.

surviving for five months in the Low Earth Orbit (LEO) have been reported. According to the presented report, the supercapacitor not only qualified for the launch [200] but could withstand different space applications, as described in Fig. 6c.

3.5. Thermal management system for space battery

The battery used for space applications, particularly planetary missions, is needed to operate in extreme conditions. For example, Venus's mission requires battery operation at high temperatures (465 °C) whereas Mars missions require low temperatures (−120 °C) condition. To maintain the proper functionality of the battery at an extreme temperature condition of space, a combination of low/high-temperature batteries along with an appropriate thermal control unit is an effective way to reduce the overall thermal management mass, size, and cost. The

battery can be operated at extreme conditions by applying heat externally or internally by the temperature control unit. Externally battery can be warmed using electrically heated thermal jackets, a sealed enclosure with an internal heating element, warm air heating, and liquid heating [202].

Jet Propulsion Laboratory, California Institute of Technology has demonstrated the thermal control [203] of Mars lander and rover batteries to keep temperatures within the −10 °C to +25 °C as shown in Fig. 7a. The lower limit of battery temperature is maintained by a phase change material (PCM) and loop heat pipe (LHP). Here, the PCM thermal storage module is used to store and release heat whereas LHP is deployed to direct heat from a set of Radioisotope Heater Units (RHUs) to the battery. In addition, the upper limit of battery temperature can be controlled by opening a thermal control valve in the LHP to regulate the fluid to an external radiator where additional heat is released to the

atmosphere.

However, external heating methods are complex and bulky, require an external power source, and are poor in efficiency (significant heat loss to the environment). Therefore, the internal heating method will be a good choice for the thermal control unit. For example, Stuart et al. developed internal heating batteries at cold temperatures using alternating currents [202]. The ongoing development and detailed description of thermal control technologies (active and passive as shown in Fig. 7b, c) for space applications can be found in the following references [204,205].

3.6. Nuclear battery

In space exploration missions, solar-powered battery systems are mainly used to provide adequate electricity to spacecraft and their instruments, which should be safe, reliable, and long life. However, the available solar intensity/flux is insufficient to generate power with photovoltaic cells for space exploration missions. Therefore, during this mission, Nuclear Batteries are mostly used with great success (Table 7). Nuclear batteries, also referred to as the Radioisotope Thermoelectric Generator (RTG), has been used in space exploration for over four decades (Fig. 8). Nuclear batteries can provide power and heat for spacecraft by converting heat generated by natural radioactive decay into electricity. RTG utilizes radioisotopes (e.g., Plutonium-238, Strontium-90) in conjunction with thermoelectric materials (e.g., Pb—Te, Si—Ge) to produce electricity and heat for decades without refuelling [206]. For example, Si—Ge uncouples in RTGs generate 280 W_e at the beginning of life (~5.5 W_e/kg) by the radioactive decay of 238Pu in 238PuO₂ fuel pellets encapsulated in the general-purpose heat source (GPHS) modules.

In RTG, the heat generated can also be used to keep various components heated. Nuclear batteries can provide high energy densities of nearly 4500 Wh/kg compared to the current lithium-ion batteries (110–160 Wh/kg) [208,209]. However, they are key challenges with RTG, such as high rejection temperature, high pressures, and high development costs for the harsh environmental conditions [21]. Department of Energy and NASA are jointly developing a new generation RTG called a Multi-Mission Radioisotope Thermoelectric Generator (MMRTG) to operate on the planetary atmosphere (Mars) and in the space vacuum. MMRTG is a flexible and efficient (6–7 %) modular design, which carries 4.8 kg of Pu-238 dioxide fuel and uses eight General Purpose Heat Source (GPHS) modules [210]. The Curiosity rover on Mars has been powered by MMRTG since Aug 2012.

Space missions are partially or totally powered by nuclear power supplies which provide a continuous source of electricity for space mission equipment for a long time. However, nuclear safety and radioactive contamination in space are major concerns in deploying these nuclear sources of energy. For example, portions of the reactor (satellite Cosmos 954) fell in Northern Canada [211]. There are also more incidents with RTG-powered missions [212]. These missions failed or exploded during launching which might cause the release of radioactive elements and part of the fine particle can be found and extend on the ground for long periods (years). However, there is a need to develop safety measures (such as enclosure of RTG isotope fuel inside high-strength graphite block surrounded by iridium metal [213]) for successive usage of RTG particularly for deep space missions where solar power generation is challenging.

4. Outlook

Batteries are an essential part of the spacecraft when considering space exploration missions. Space operations and all the electronics, scientific equipment, and communications largely depend on the on-board battery power. Li-based primary batteries with high specific energy displays promise to be used as a power source in deep space exploration missions under extreme operating conditions.

Table 8

Battery chemistry deployed in different space missions.

S. N.	Mission	Launch year	Destination	Battery System
1	Vanguard	1956	Earth satellite	Zn-Hgo
2	Earth science (Explorer 1)	1958	Earth orbit	Zn-HgO
3	Earth science (Explorer 6)	1959	Earth orbit	Ni-Cd
4	IMP-1	1961	Earth orbit	Ag-Cd
5	Ranger-3	1962	Solar orbit	Ag-Zn
6	Ariel 1	1962	LEO	Ni-Cd
7	Gemini	1962	Moon	PEM Fuel cell
8	Mariner-2	1962	Venus	Ag-Zn
9	Mariner-4	1962	Mars	Ag-Zn
10	Mariner-5	1962	Venus	Ag-Zn
11	Syncom-2	1963	Earth orbit	Ni-Cd
12	NTS-2	1966	Earth orbit	Ni-H ₂
13	USAF	1966	Earth orbit	Ni-H ₂
14	Biosatellite	1967	Earth orbit	PEM Fuel cell
15	Lunar Orbiter	1967	Moon	Ni-Cd
16	Apollo 7	1968	Earth orbit	Alkaline Fuel cell
17	Mariner 9	1972	Mars	Ni-Cd
18	Viking-1	1975	Mars	Ni-Cd
19	Viking-2	1975	Mars	Ni-Cd
20	Solar Max	1980	Solar orbit	Ni-Cd
21	Shuttle (STS-1)	1981	Earth orbit	Alkaline Fuel cell
22	Intelsat V	1983	Geostationary orbit	Ni-H ₂
23	STS-3	1983	Earth orbit	Li-BCX
24	Long Duration Exposure Facility	1984	Earth orbit	Li cells
25	Galileo	1989	Jupiter	Li-SO ₂
26	Hubble Space Telescope	1990	Space	Ni-H ₂
27	Leasat	1990	Space	Ni-Cd
28	Clementine	1994	Moon	Ni-H ₂
30	Centaur	1995	Alpha Centauri A and B	Li-SOCl ₂
31	Iridium-1	1996	Earth orbit	Ni-H ₂
32	Mars Observer	1996	Mars Orbiter	Ni-Cd
33	Mars Global Surveyor	1996	Mars	Ni-H ₂
34	Flight Experiment	1997	Earth orbit	Na-S
35	Mars Climate Orbiter	1998	Mars	Ni-H ₂
36	Genesis	2000	Solar	Li-SO ₂
37	Mars Odyssey	2001	Mars	Ni-H ₂
38	Mars Surveyor Program Lander	2001	Mars	Li-ion
39	Countour	2002	Mars	Ni-Cd
40	Deep Impact	2002	Comet	Li-SOCl ₂
41	Beagle-2 Lander	2003	Mars	Li-ion
42	Mars Express	2003	Mars	Li-ion
43	Mars Exploration Rovers	2003	Mars	Li-ion
44	MER-Spirit	2003	Mars	Li-ion
45	MER-Opportunity	2003	Mars	Li-ion
46	Messenger	2004	Mercury	Ni-H ₂
47	Cassini-Huygens	2004	Saturn	Li-SO ₂
48	Deep Impact	2005	Comet	Ni-H ₂
49	Mars Reconnaissance Orbiter	2005	Mars	Li-ion
50	New Horizons	2006	Pluto	No Battery
51	Phoenix Lander	2007	Mars	Li-ion
52	Dawn	2007	Vesta & Ceres	Ni-H ₂
53	Kepler	2009	Earth Orbiter	Li-ion
54	Mars Science Laboratory	2009	Mars	Li-ion
55	Lunar Reconnaissance Orbiter	2009	Moon	Li-ion
56	LCROSS	2009	Moon	Li-ion
57	Juno	2011	Jupiter	Li-ion
58	GRAIL	2011	Moon	Li-ion
59	Crew Exploration Vehicle	2012	Moon	Li-ion
60	Crew Launch Vehicle	2012	Moon	Li-ion
61	LADEE	2013	Moon	Li-ion

(continued on next page)

Table 8 (continued)

S. N.	Mission	Launch year	Destination	Battery System
62	MAVEN	2013	Mars	Li-ion
63	OSIRIS-Rex	2016	Asteroid	Li-ion
64	InSight	2018	Mars	Li-ion
65	Mars 2020	2020	Mars	Li-ion
66	Deep Space Climate Observatory	2015	L-1	Li-ion
67	Magnetospheric Multiscale Satellites	2015	Various Orbits	Li-ion
68	Transiting Exoplanet Survey Satellite	2017	HEO Orbit	Li-ion
69	James Webb Space Telescope	2018	L-2	Li-ion
70	JPS2	2021	LEO	Li-ion

Table 9

Li-ion battery electrode chemistry used in space application.

	Cycle life	Calendar life	Specific Energy	Safety	Mission
Cathode					
LiNi _{0.8} Co _{0.2} O ₂	Good	Good	Moderate	Moderate	Juno, MAVEN
LiCoO ₂	Good	Good	Moderate	Moderate	Lcross, Dscovr
LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	Excellent	Excellent	High	Good	InSight, Mars-2020
Anode					
Hard Carbon	Good	Good	High	Good	Kepler, Proba
MCMB	Excellent	Excellent	Moderate	Moderate	Opportunity

The rechargeable batteries are charged by solar photovoltaics when sunlight is available, and their power is utilized to complete the mission objectives. The intensity of sunlight reduces as we move farther away from the sun, implying that the outer planets of the solar system would be much colder than the inner. The spacecraft with targeted missions on the outer planets would have a nuclear battery system (MMRTG) to power it up. Nonetheless, batteries are an integral part of any extra-terrestrial missions to power the spacecraft that space agencies plan. However, looking at the current state of the art in the development of batteries; rechargeable and nuclear batteries will be the more promising battery technology over primary batteries. In these battery systems, Ag—Zn rechargeable batteries are useful for short-term space applications such as launch vehicles and powering critical units like the extravehicular mobility unit. Ni—Cd batteries are a good choice for the various space orbital missions (e.g., LEO and GEO) due to their good cycle and calendar life. However, the Ni—H₂ system almost has the same performance as the Ni—Cd system, but it has higher cycle life for the same DOD. Thus, it replaced Ni—Cd chemistry where the power requirement is >1 kW, such as in high-power GEO applications.

The utilization of rechargeable batteries such as silver-zinc (Ag—Zn), nickel-cadmium (Ni—Cd), nickel-hydrogen (Ni—H₂), and lithium-ion (Li-ion) have been increasing in space missions [8,11] as shown in Table 8.

However, Li-ion rechargeable batteries are the ultimate choice for most of the space applications where mass and volume requirements are critical with moderate cycle life. Table 9 provides the comparative characteristics of different Li-ion battery electrode chemistry deployed in space applications.

Most Li-ion battery cells deployed in space applications used meso-phase carbon microbeads (MCMB) and hard carbon (e.g., EnerSys/ABSL space batteries) as an anode material with metal oxides cathodes such as

LiCoO₂, LiNiCoO₂, and LiNiCoAlO₂ (Table 9). Recently, LIBs based on MCMB anode and LiNixCo_{1-x}O₂ (NCO) cathode have been employed in the rover sent by NASA on the Martian exploration mission to meet the energy requirement during peak rover activities.

The current development of Li-ion battery electrode chemistry (anode and cathode) can play a vital role in the development of space applications. Particularly, alloy-based anode (Si, Ge, Sn) can deliver high energy density of the battery and reduce the launch payload and cost. Furthermore, the Lithium titanate (LTO) anode will be an excellent selection for spacecraft applications (e.g., LEO radar satellites) due to its long cycle life and high-rate capability. Furthermore, the LiFePO₄-based cathode electrode will be suitable electrode material for outer planetary missions due to its excellent safety, high-rate capability, and long-term cycle and stability up to 400 °C. The use of flexible lithium-ion batteries will be a promising way to achieve high volumetric energy density for extravehicular activity applications. The ternary mixtures of EC, DEC, and DMC will be the preferred combination at a low-temperature performance of Li-ion cells for space exploration of inner/cold planets with the advanced thermal control unit. Further, the solid electrolyte (e.g., LAGP, LLZO) eliminates flammable liquid electrolytes and safety systems, thereby increasing the energy density even in extreme operational conditions. However, further research needs to be focused on Li-ion cells to improve their performance, particularly in extreme conditions (low and high temperatures) with advanced development in the thermal management system.

Beyond lithium-ion batteries, such as Li—S, Li-air, Li-CO₂, and other battery chemistries hold great promises because of the high specific capacity of lithium 3842 mAh/g. For example, Patrick et al. [218] developed an all-in-one lithium-sulfur battery where the lithium and sulfur are infused in the porous-dense-porous tri-layer of garnet as a solid-state electrolyte. The unique all-in-one cell design exhibits all the necessary attributes and yields a high capacity of 1200 mAh/g with nearly 100 % coulombic efficiency. The utilization of solid electrolytes eliminates the safety concerns and enables higher loading of lithium and sulfur as electrode materials, leading to a practical high energy density of 272 Wh/kg. LiO₂/Li₂O₂ inter-conversion-based positive electrode architecture has been shown to demonstrate a practical energy density of 500 Wh/kg in a pouch cell with Li-metal as the counter electrode. Qiao et al. [219] developed a unique composition of cathode material by compositing LiO₂ with a Ni-based catalytic framework to deliver such remarkable energy density. This work provides a benchmark in developing emerging electrode systems and their translation into practical pouch-cell format relevant to technological advancements. However, the working mechanism of such an electrode system is still unclear, and further research is needed to elucidate the same in which the system works [219,220]. The Nano Diamond Battery, developed by a California-based NDB company, utilizes radioactive wastes (C-14) to generate electricity encapsulated in an artificial diamond case. The company claims that this battery can deliver electricity for thousands of years. The large-scale application of nano-diamond batteries could power satellites and interplanetary missions [221]. Plentiful research must be directed towards developing these types of batteries, as they could be utilized for extreme operating conditions envisioned for future planetary missions and have the potential to go where no battery has gone before. However, their fundamental scientific challenges and their feasibility in space missions further need to be explored (Fig. 9) with advanced electrochemical characterization (polarography, voltammetry, electrogravimetry, coulometry, and potentiometry [222], ex-situ or in-situ operando techniques (X-ray techniques, electron microscopy, Raman spectroscopy [216,223]), simulation techniques (density functional theory, molecular dynamics, monte carlo, phase field method, finite element method) and machine learning approach (prediction, screening, optimization [215])).

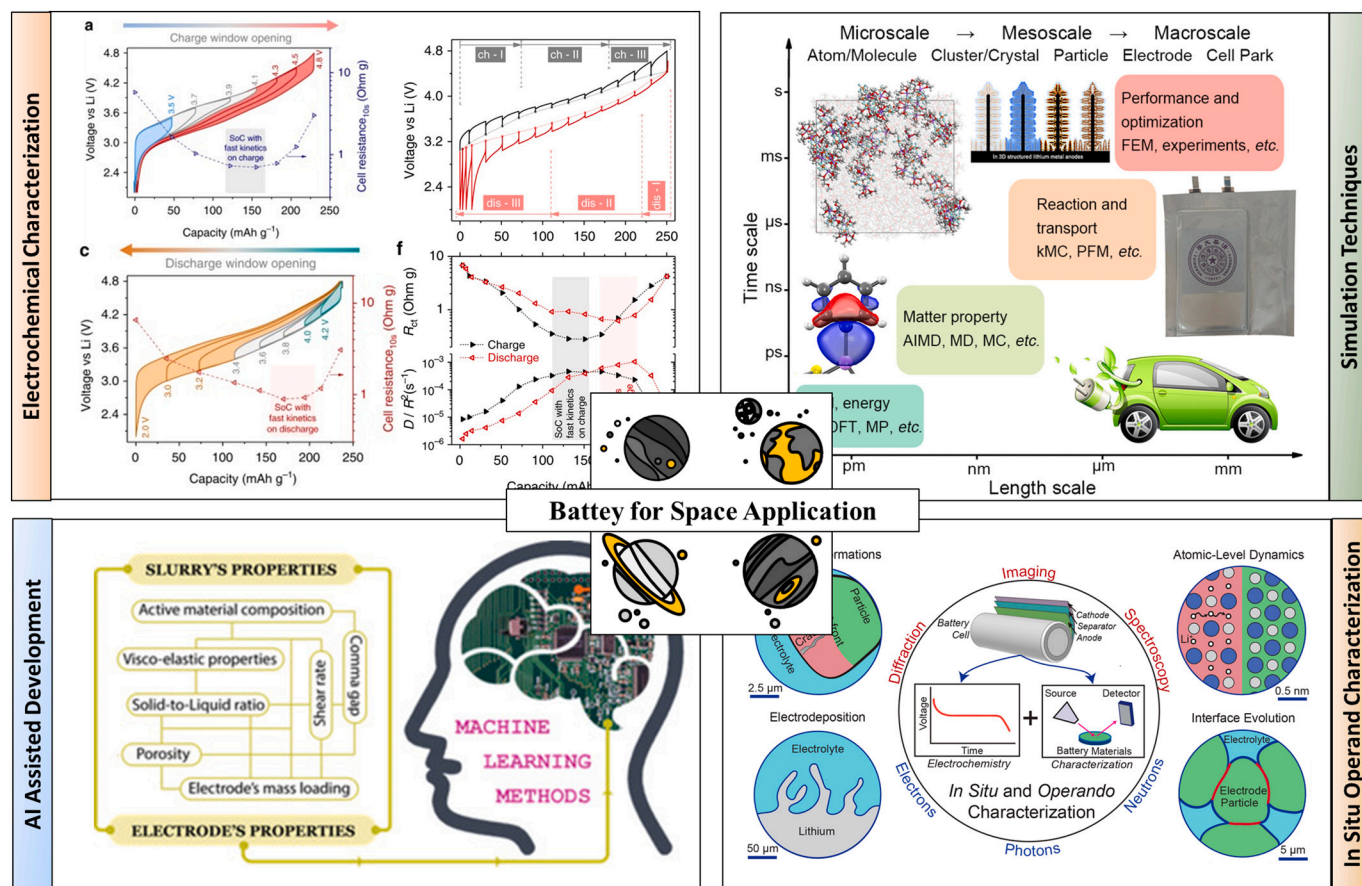


Fig. 9. Schematic of showing the way forward for the development of battery technology with electrochemical characterization. Reproduced with permission [214]. Copyright 2017, Springer Nature. Simulation techniques. Reproduced with permission [215]. Copyright 2021, Wiley. In-situ operand characterization. Reproduced with permission. [216], Copyright 2019, American Chemical Society. and AI development. Reproduced with permission [217]. Copyright 2021, Wiley.

Declaration of competing interest

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Data availability

No data was used for the research described in the article.

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