

Elijah Haga

Mr. Cost

A.P. Chemistry

June 13, 2024

A Study on Lithium-Ion Batteries

Abstract

Recent years have seen many advances in rechargeable batteries, especially lithium-ion batteries. Lithium-ion (or Li-ion) batteries are notable for their large reduction potential and high energy density, making them ideal for compact electronic devices. In this study, a lithium-ion battery was fabricated using low-temperature lithium cobalt oxide (LT-LiCoO₂) as the cathode, graphite (C) as the anode, and lithium perchlorate (LiClO₄) dissolved in dimethyl-carbonate (C₃H₆O₃) as the electrolyte. Polytetrafluoroethylene (PTFE) was used as the binder to hold the electrode materials together and carbon black was used as a conducting agent to improve the cell's conductivity. The cell created had a potential difference of +3.2 V, which was measured using a BK Precision 20 Mhz Oscilloscope Model 2120.

Introduction

Electrochemistry is the study of how electricity and chemical reactions relate. There are two types of electrochemical cells: electrolytic and galvanic. Both use reduction-oxidation

(REDOX) reactions, where one substance transfers electrons to another. Galvanic cells use a thermodynamically favored chemical reaction to create electricity. Electrolytic cells do the opposite, using electricity to make a non-thermodynamically favored reaction occur. By using substances that work in both types of cells, a rechargeable battery can be created, where the battery acts as a galvanic cell when discharging and an electrolytic cell when charging.

Galvanic and electrolytic cells require a few key components to operate. Both types of cells require two electrodes: a cathode, which is the substance being reduced (gaining electrons), and an anode, which is the substance being oxidized (losing electrons). These electrodes are connected with a wire to allow electrons to transfer between them. When the atoms in the anode lose electrons, they become charged ions and are released into an electrolyte solution. In a galvanic cell, a salt bridge is required, where an aqueous salt solution is connected to both sides so that the ions can balance out the ions released during the cell's operation. In an electrolytic cell, a power supply must be included to supply the energy required for the chemical reaction to occur. To make a rechargeable battery, however, the power supply must be removable, or else the battery is purposeless. Combining all these components, we can create an electrochemical cell that operates as an electrolytic cell to charge, and then as a galvanic cell to store and discharge electricity.

Although many substances have been used in rechargeable batteries in the past, the most commonly used rechargeable batteries currently are lithium-ion (Li-ion), nickel-cadmium (NiCd), nickel-metal hydride (NiMH), and lead-acid (Pb). However, all these batteries currently suffer from poor recycling practices or reliance on hazardous chemicals that could be dangerous if released (Zubi et al., 2018). Lithium-ion batteries are incredibly energy-dense, making them the most common choice for electronics, where compactivity is essential. As the name suggests,

they operate by transferring lithium ions between the cathode and the anode to generate electricity. This generates a large potential difference, but it means the anode and the cathode must be able to accept and release lithium ions. Due to the high reactivity of pure lithium, it is rarely used as an electrode. Instead, lithium compounds such as lithium cobalt oxide (LiCoO_2), lithium manganese oxide (LiMn_2O_4 , Li_2MnO_3 , LiMnO_2 , or Li_2MnO_2), and lithium nickel manganese cobalt oxide ($\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$) are used as cathodes to mitigate the risk of explosion or combustion, however, these materials have much lower conductivity and higher impedance than raw lithium. Likewise, anodes are typically graphitic carbon (C), hard carbon (C), lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$), and silicon-based materials (Mishra et al., 2018). Basu et al. (1979) demonstrated the ability of lithium to intercalate into graphite (Fig. 1.), which Rachid Yazami & Touzain (1983) proved to be reversible. This meant that lithium ions could be accepted by a graphite electrode, enabling graphite to be used as an anode of lithium-ion batteries. It is now the most commonly used anode for such batteries due to its low cost and ease of production. New anodes based on silicon are being researched, which may experience less degradation than a typical graphite anode.

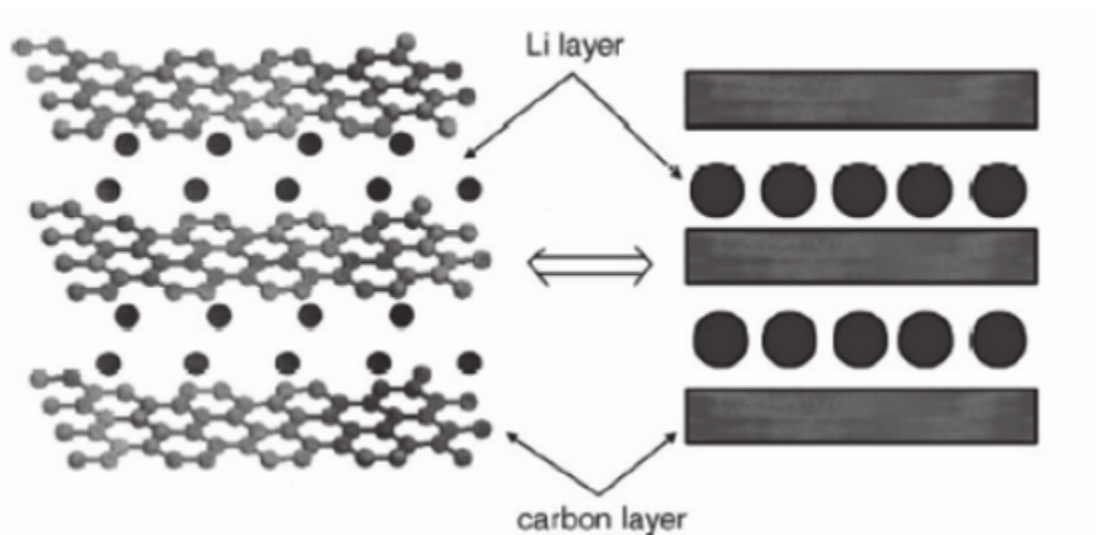


Fig. 1. Schematic design showing the intercalation of lithium ions into graphite (Sur, 2011).

For lithium-ion batteries to operate properly, additional materials must be included. To allow lithium ions to flow between the electrodes without short-circuiting the cell, a separator must be introduced which is permeable to lithium ions but does not conduct electricity. The most common substances used as a separator are polyethylene ($(C_2H_4)_n$) and polypropylene ($(C_3H_6)_n$) as if the cell heats up too much, which is a sign of thermal runaway, these substances melt. This halts ion flow, preventing the battery from operating and causing further damage such as combustion or chemical leakage. For ions to flow, an electrolyte such as lithium perchlorate ($LiClO_4$) must be dissolved in an organic solvent such as ethyl-methyl-carbonate ($C_4H_8O_3$), dimethyl-carbonate ($C_3H_6O_3$), or diethyl-carbonate ($C_5H_{10}O_3$). Due to their high impedance and low conductivity, the lithium compounds must be finely powdered and blended with a conducting agent, typically carbon black. Carbon black acts like bits of graphene, having a high conductivity but high spreadability. A binder, such as polytetrafluoroethylene (PTFE), and a

solvent, such as isopropanol ($\text{C}_3\text{H}_8\text{O}$), are added to this mixture so that the cathode can be shaped and applied in a thin coating to a substrate, typically aluminum foil, using a doctor blade or spatula. This substrate acts as a current collector so that all particles in the cathode can participate in the cell's reaction. The anode is prepared very similarly, using graphite powder, carbon black as a conductive agent, PTFE as a binder, and isopropanol as a solvent, but copper foil instead of aluminum foil as a substrate (Zubi et al., 2018; OpenAI, 2024).

When creating a lithium cobalt oxide electrode, it is important to consider the two discovered variations: low-temperature lithium cobalt oxide (LT-LiCoO₂) and high-temperature lithium cobalt oxide (HT-LiCoO₂ or O3-LiCoO₂). While HT-LiCoO₂ is prepared around 850°C using sintering and has a rhombohedral, layered structure, LT-LiCoO₂ is prepared around 400°C using various other methods such as hydrothermal or sol-gel and has a spinel structure of Li₂Co₂O₄. The spinel structure blocks lithium ions from entering and exiting the LT-LiCoO₂ electrode, as shown in Fig. 2. This means that LT-LiCoO₂ has worse electrochemical properties, with a lower potential difference and weaker current (Julien et al., 2015).

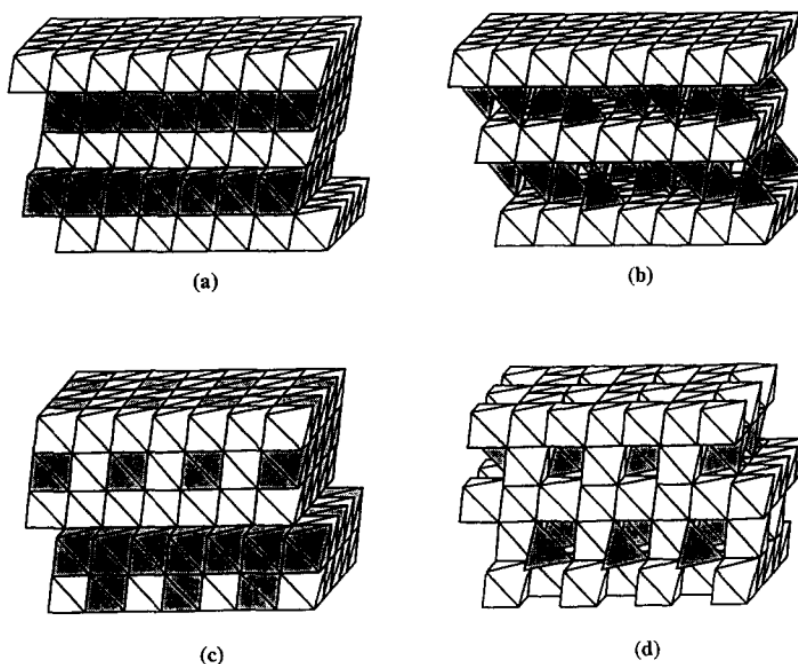


Fig. 2. “Idealized structures of (a) LiCoO_2 layered, (b) $\text{Li}_{0.5}\text{CoO}_2$ layered, (c) $\text{Li}_2\text{Co}_2\text{O}_4$ spinel, and (d) LiCo_2O_4 spinel. Unshaded and shaded polyhedra contain Co and Li, respectively” (Gummow et al., 1993).

Despite the many advantages of lithium-ion batteries, there are a few major disadvantages to their use, especially regarding how their materials are collected. Lithium mining occurs either through the evaporation of brine or by crushing rocks containing lithium. Both of these processes devastate ecosystems as high-volume mining kills local plant and animal life. Additionally, lithium and cobalt are very limited resources, making lithium-ion batteries a non-sustainable good. Lithium-ion batteries also degrade over time as charging the battery converts some of the lithium ions intercalated into the graphite to turn into lithium metal, preventing them from transferring back to the cathode. When this happens, the lithium metal

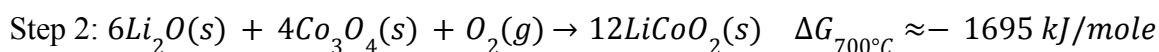
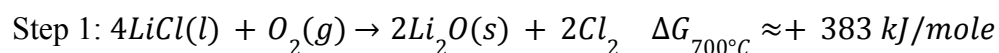
becomes trapped, meaning it can no longer be used in the operation of the cell. This process slowly eats away at a battery's charge capacity over time, eventually reducing it to the point of uselessness (Davies, 2024). As recycling these batteries is difficult, with only ~90% purity of recovered materials, once the lithium deposits run out, other batteries and materials must be used (Methekar & Anwani, 2018). Hopefully, with innovations in battery development and more research, other batteries will be developed that do not rely on materials such as lithium that must be mined (Institute for Energy Research, 2023; MIT Climate Portal, 2024).

To test these battery fundamentals, a lithium-ion battery was fabricated. A lithium cobalt oxide (LiCoO_2) cathode and graphite (C) anode were created as these materials have been extensively researched, with lithium cobalt oxide being the first commercial lithium-ion battery developed by Rachid Yazami and John B. Goodenough in 1991 (Bhatt et al., 2016). These electrodes were connected with a polyethylene ($(\text{C}_2\text{H}_4)_n$) separator soaked in lithium perchlorate (LiClO_4) to allow lithium ions to flow between the two. The voltage between the two electrodes was measured using an oscilloscope during its operation.

Procedure

20.00 grams of cobalt (ii, iii) oxide (Co_3O_4), 10.56 grams of lithium chloride (LiCl), 10.00 grams of graphite (C), 2.00 grams of polytetrafluoroethylene (PTFE), 2.00 grams of carbon black (C), isopropanol ($\text{C}_3\text{H}_8\text{O}$), aluminum foil, copper foil, polyethylene soaked in lithium perchlorate (LiClO_4), an evaporating dish, two crucibles with lids, a mortar and pestle, wire gauze, a bunsen burner, a drying oven, a vacuum aspirator, a sheet of filter paper, two 100 mL beakers, and a spatula were obtained.

To create the lithium cobalt oxide (LiCoO_2) cathode, a unique method described by Khoklov et al. (2014) was used. This method makes use of a coupled reaction (Eq. 1.) to fabricate lithium cobalt oxide at 700°C using lithium chloride and cobalt (ii, iii) oxide.



Eq. 1. Equation describing the fabrication of lithium cobalt oxide at 700°C (Khoklov et al., 2014)

Although the first step of this reaction is thermodynamically unfavored, meaning it will not occur spontaneously, the high thermodynamic favorability of the second step makes the overall reaction occur. To prepare the cobalt (ii, iii) oxide and lithium chloride for their synthesis, both were placed in a crucible and heated over the Bunsen burner for 2 hours to remove any water. Following their drying, all of the cobalt (ii, iii) oxide and lithium chloride were poured into the evaporating dish. The mixture was heated over the Bunsen burner for 8 hours inside a fume hood. The fume hood was used to prevent the chlorine gas that the reaction emitted from escaping while providing oxygen through the surrounding air, but was kept off so it would not cool the mixture. The resulting material, lithium cobalt oxide powder, was suspended in distilled water to remove impurities and to obtain as much of the product as possible (Khoklov et al., 2014). This suspension was filtered through the vacuum aspirator using a sheet of filter paper. After drying for 10 hours, 10.00 grams of the lithium cobalt oxide were separated. 1.00 grams of the PTFE and 1.00 grams of the carbon black were measured out and added to the lithium cobalt oxide. This mixture was stirred until it was homogeneous, then isopropanol was slowly added and the solution was stirred until the mixture was thoroughly wetted. A 4-inch by 2.5-inch

rectangle of aluminum foil was cut out and the mixture was placed on top. The mixture was then evenly spread across the surface of the foil with the spatula, ensuring that the mixture had a uniform thickness. This electrode was dried in a drying oven at 110°C for 2 hours to evaporate all of the isopropanol (OpenAI, 2024).

To create the graphite anode, much of the process of creating the anode was repeated. A graphite electrode was pulverized into a powder using a mortar and pestle, and 10.00 grams of the resulting powder was measured out and separated. 1.00 grams of PTFE and carbon black were added to the 10.00 grams of graphite powder, and the mixture was stirred until it was homogeneous. Isopropanol was gradually added as the mixture was stirred until the mixture was thoroughly wetted. A 4-inch by 2.5-inch rectangle of copper foil was cut out and the graphite mixture was spread out on its top using the spatula (which had been cleaned after its use on the anode), making sure that it had a uniform thickness. This electrode was also dried in the drying oven at 110°C for 2 hours to evaporate all of the isopropanol.

To create the separator and electrolyte, lithium perchlorate or lithium hexafluorophosphate (LiPF_6) was necessary to act as an electrolyte (Li et al., 2016). However, both of these substances are difficult to manufacture. Producing lithium perchlorate requires either electrolysis of a chlorate, such as sodium chlorate (NaClO_3), using a titanium electrode or a double replacement reaction between a lithium substance and a perchlorate, such as potassium perchlorate (KClO_4) (Lifei et al., 2021; Hampel & Leppla, 1947). Producing lithium hexafluorophosphate requires numerous other chemicals and reactions, many of which are difficult to produce, such as phosphorus pentachloride (PCl_5) (Doucan et al., 2003). As both of these methods were unviable, the electrolyte was instead obtained from a commercial lithium-ion battery. The battery was discharged and carefully deconstructed, and the separator soaked in

electrolyte and organic solvent was removed. This separator was used in the cell produced, meaning the electrolyte and organic solvent were already incorporated into the cell.

A wire was connected to the anode and was soldered to a 220 Ω resistor. The resistor was soldered to an LED, which was in turn soldered to a wire that could be connected to the cathode easily. A probe from the oscilloscope was attached to the wire so that the voltage and signal could be monitored during the battery's lifecycle. The anode was placed powder-side up and the separator was placed on top of it, making sure that it completely covered the lithium cobalt oxide. The cathode was placed on top of the separator, making sure that none of the graphite powder went over the separator. The wire was connected to the cathode, and the cell was allowed to operate.

Results and Analysis

The lithium-ion battery produced had a potential difference of +3.2 V, as measured by an oscilloscope. It lit the LED as well, proving that the cell was operating correctly. However, about 7 seconds into operation, a popping sound was heard, a spark arced between the electrodes, and the cell caught on fire. A fire extinguisher was used to put out the fire, but this destroyed the cell. While the cell was functional, poor construction resulted in its failure, highlighting the difficulty in producing lithium-ion batteries and the importance of safety regarding them.

The measured voltage is consistent with other lithium-ion cells, matching the voltage of the LT-LiCoO₂ battery produced by Gummow et al. (1993). This suggests that the lithium cobalt oxide produced was LT-LiCoO₂ and that the cell operated correctly until its failure.

To improve the fabrication of the cell and to increase its supplied voltage, a hydrothermal method would have been preferred, however, the lack of necessary materials prevented the use of this method. A hydrothermal production of lithium cobalt oxide can be performed using cobalt (ii) hydroxide ($\text{Co}(\text{OH})_2$) and lithium hydroxide (LiOH) as precursors, lithium hydroxide/sodium hydroxide (NaOH) as mineralizers, and hydrogen peroxide (H_2O_2) as an oxidant. Such a method requires consistent heating over long periods but produces very pure lithium cobalt oxide (Bokinala et al., 2013). Alternatively, sintering could have been used to produce high-performance HT- LiCoO_2 , but such a method requires extremely high temperatures (usually 800°C or higher) and many difficult-to-produce chemicals (Kim et al., 2012).

Another way to increase the voltage, capacity, and lifecycle of the cell would be by obtaining a thinner, more uniform layer of lithium cobalt oxide and graphite on the electrodes (Zheng et al., 2012). To achieve a thinner, more uniform layer on the electrode, techniques such as air spraying, electrostatic spraying, and hot/roller pressing are utilized. These methods can improve the bonding strength of the powder to the foil by 64.5 kPa and the charge retention by 12% as opposed to a slurry-cast electrode like the one created in this experiment (Zhang et al., 2024).

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