

# School Experiments on Different Lithium Batteries

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**Abstract** Lithium-ion based batteries are the most commonly used energy storage systems for electronic systems like tablets, smartphones, etc. in present times. Moreover, lithium ion-batteries are “the beacon of hope” for the automotive industry for the use in electric and hybrid cars and for the energy revolution to be applied as a short-time energy storage. However, other lithium-metal-based batteries are used in everyday life, such as lithium-manganese dioxide battery or lithium-iodine-battery. These types of batteries are much less known, but are used very frequently in everyday life. In this article simple experiments with lithium-batteries are presented.

**Keywords:** *lithium batteries, lithium-manganese dioxide-batteries, lithium-pyrite-batteries, lithium-iodine-batteries*

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## 1. Introduction

Lithium-batteries currently available are primary cells, comprising metallic lithium as anode material. The standard potential of metallic lithium is  $-3,05$  V leading to a high cell voltage [1,2] especially if combined with a suitable cathode material. Another advantage is, that the inevitable corrosion products that forms on the lithium metal surface can be passed by the lithium ions. Due to the obvious fact that metallic lithium cannot be used in aqueous solutions, organic solvent such as dimethyl carbonate, propylene carbonate or dimethoxyethane or mixtures thereof are used as solvents for the electrolytes, such as lithium perchlorate, e.g. [3].

The most popular metallic lithium batteries are those that use manganese dioxide as the cathode material in the known form of the alkaline zinc-manganese dioxide cells or in the form of a button cell. The lithium-iodine battery is used in cardiac pacemakers because of its long life. A curiosity is the lithium pyrite battery, which replaces the zinc-manganese dioxide cells especially in the field of photography with a cell voltage of only  $1,5$  V [4,5].

The battery systems presented here are not rechargeable like the lithium-ion-battery. However, research is focusing on lithium-oxygen- and lithium-sulphur-batteries, which could be used as accumulators in future [6-8]. For the automotive industry, these batteries are “the beacon of hope” for the use in electric and hybrid cars to be applied as a suitable energy storage system.

Pyrite, an iron-sulphur compound, is another notable candidate as an electrode material in a lithium-pyrite battery with a battery voltage (without electrical load) of  $3,54$  V [9].

## 2. Didactic Explanation

An important task of chemical education is to prepare and educate pupils in the fields of technologies, their use and problems, concerning nowadays and tomorrows energy storage systems like batteries and accumulators.

It is often shown, that with a technological breakthrough, a lot of problems have to be solved, which can be illustrated via the example of the research and commercial viability of the lithium-metal battery. These topics have to be addressed in chemical education and there is a need for straightforward experiments which illustrate why some lithium-metal batteries are suitable for one purpose and unsuitable for another [10].

These topics aren't taught normally via experiments. Therefore, a development of suitable and easy to do experiments and materials concerning lithium-ion-batteries is of great importance. Such work has been done for the lithium-ion-accumulator by the working group OETKEN ET AL. [11,12,13]. In the following article, the aim of the experimental understanding of the lithium metal batteries already used in everyday life is to explain with simple experiments why these are only suitable for certain purposes. For this, the aforementioned battery systems for the use in laboratory trainings in higher education and upper secondary school. These simple experiments on everyday lithium-metal batteries differ from the experimental work on lithium-ion batteries by the working group Oetken, as they deal with lithium-metal instead of lithium-ion technology.

It is also shown why the lithium-metal batteries presented here are suitable as mono cells, but are unusable as large-scale storage systems for electromobility and the

energy transition. Oxygen-based metal batteries, such as the lithium-metal-oxygen battery, seem to be much more suitable for this. It will present suitable experiments like it has been shown for the lithium metal-oxygen-battery [14].

### 3. Common Lithium Primary Batteries

Besides the popular lithium-ion accumulator, there exist a number of lithium-ion-batteries and metallic-lithium-batteries in our everyday life. The lithium-manganese dioxide battery, lithium-pyrite-battery and lithium-iodine-battery are already commercially available. Their electrochemical processes and performance can be easily demonstrated via suitable and straightforward experiments on a laboratory scale.

#### 3.1. The Lithium-Manganese Dioxide-battery

The most common metallic-lithium-battery at the moment is the lithium-manganese dioxide battery. It is a primary cell which is sold as a mono cell as well as a button cell (e.g. Figure 1). On top of the button cell, its specification is given, CR 2016, for example. The given letters CR stand for a round cell with lithium as the negative electrode. The numbers indicate the dimension of the cell, with a diameter of 20 mm and a thickness of 1,6 mm [4].



Figure 1. Representation of a lithium-manganese dioxide battery (button cell - own picture taking)

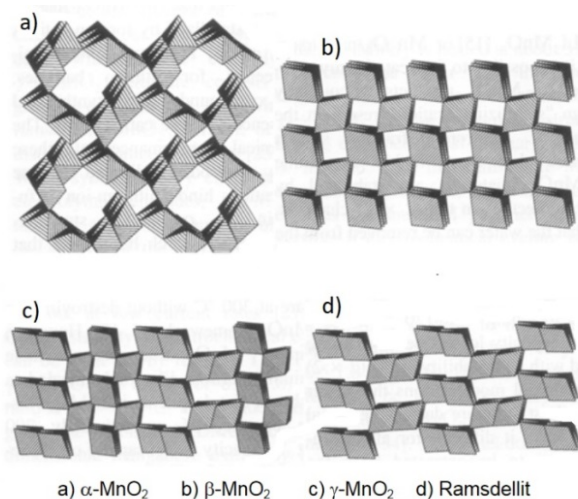


Figure 2. Structure of manganese dioxide [16]

A lithium-manganese dioxide battery possesses a voltage between 3,0 V to 3,5 V [15,16]. For the electrolyte solution, lithium perchlorate is dissolved in organic solvents, like dimethyl carbonate, propylene carbonate, dimethoxyethane, or similar compounds. In order to increase the electric conductivity, dispersed carbon is added to the manganese dioxide. The manganese dioxide used has to meet a specific requirement: it has to be in its  $\gamma$ -modification (e.g. Figure. 2).

The commercially available manganese dioxide is present in its  $\gamma$ -polymorph, but it contains water. But in order to construct a lithium-manganese dioxide battery, in particular the electrolyte, has to be free from water. Therefore, the manganese dioxide has to be dried via heating before use. But through heating arises a new problem: if heated above 200 °C for a longer period of time, it can change to the  $\beta$ -modification. DIERKS AND VENNEMANN [4] recommended as early as 2005, to put a mixture of 5 g manganese dioxide and 1 g finely powdered charcoal in a crucible in a microwave for 30 s at 800 W according to the method presented by LÜHKEN AND BADER [17]. (Caution: heating the mixture is crucible for an extended period of time can lead to glowing of the mixture!).

Using this method leads to an evaporation of the water in the manganese dioxide without leading to a structural change. But even with this treated mixture of manganese dioxide and charcoal, DIERKS AND VENNEMANN were unable to build up a lithium-manganese dioxide battery which was capable of operating an electric motor. Nevertheless, is this method used and improved in course of the following experiment.

##### 3.1.1. Experiment: lithium-manganese dioxide battery

*Used equipment:* cone-shaped clay pot (height = 7 cm,  $\text{Ø} = 1,7$  cm), pencil lead as a collecting electrode with a diameter of  $\text{Ø} = 6.5$  mm (Faber-Castell Nr. TK9071), 150-mL-beaker, 2 multimeters (voltmeter and amperemeter), cable material and crocodile clips, sensitive electric motor (starting voltage 0,2 V and amperage 2-5 mA), powerful electric motor (starting voltage 0,4 V and amperage 8-20 mA)

*Used chemicals:* Lithium metal (lithium wire, e.g., GHS02, GHS05, source of supply: sigma Aldrich Nr. 278327-25G), manganese dioxide (GHS08, GHS07), lithium perchlorate (GHS02, GHS07), dimethyl carbonate (GHS02), propylene carbonate (GHS07), finely ground activated carbon

##### *Preparation:*

a) For the electrolyte solution 10 g of lithium perchlorate are dissolved in a mixture of 60 ml of dimethyl carbonate and 40 ml propylene carbonate. For better solubility, the solution should be stirred with slight warming.

b) For the lithium-manganese dioxide-battery a mixture of 5 g manganese dioxide and 1 g activated carbon are finely ground.

*Procedure:* The manganese dioxide activated carbon mixture is put into a porcelain crucible and heated for 30 s at 800 W in a microwave. The mixture is transferred into a

cone-shaped clay pot, in which a pencil lead is put beforehand. The pencil lead serves as a collecting electrode. The clay pot is stored in an exsiccator to keep it dry. A beaker is filled with approximately 75 mL electrolyte solution prepared as described in preparation a. A piece of lithium wire with a length of approximately 3 cm is freed of its possible crust. The lithium oxide layer can be removed with a spatula or knife. The lithium metal should then be flattened with a spatula or knife for a larger electrode surface. It is held via a crocodile clip and put 2 cm into the solution. The mixture in the cone-shaped clay pot is moistened with a few milliliters of the electrolyte solution and then the whole cone-shaped pot is put inside the beaker (cf. Figure 3 for the whole experimental setup). At first the voltage without electrical load is measured and afterwards an electric motor is included into the circuit. The voltage and current are measured via the amperemeter and voltmeter. At the end, the voltage without electrical load is measured again. When required one can determine the potential of each half cell under electrical load and without electrical load.

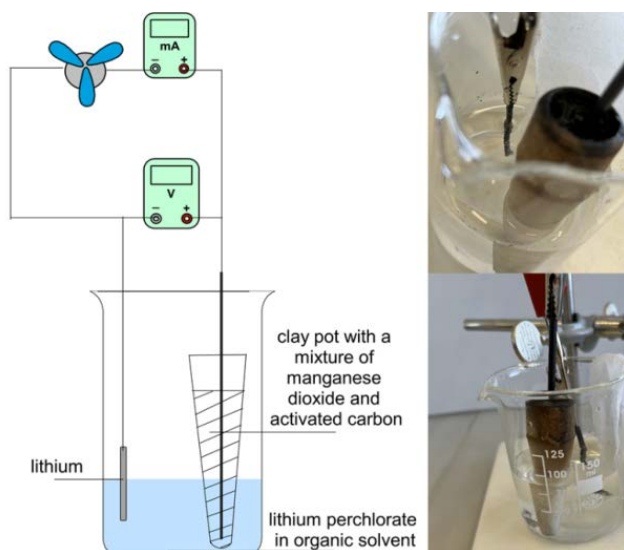


Figure 3. Experimental setup for the lithium-manganese dioxide-battery

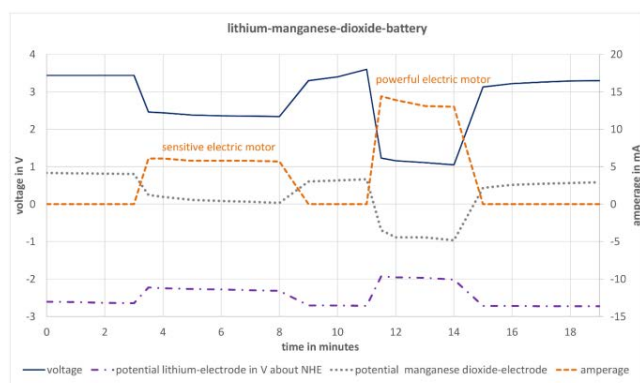


Figure 4. Measured voltage, current and potentials of the lithium-manganese dioxide-battery

**Results:** At the beginning of our experiment, the voltage of the battery (without electrical load) was measured at almost 3,44 V, the resting potential of the lithium electrode is at  $-2,64$  V and the manganese dioxide electrode at  $+0,80$  V. After integration of the electric

motor in the circuit the propeller was rotating very fast. The electric motor consumed a current of 6 mA. The voltage dropped to 2,4 V. The potential of the lithium electrode remains stable at  $-2,27$  V whereas the potential of the manganese dioxide electrode is at approximately 0 V. After a period of 5 minutes with a running motor, the voltage is at 3,5 V. The resting potential of the lithium-electrode changed a bit, compared to the start, to  $-2,71$  V whereas the resting potential of the manganese dioxide electrode is at  $+0,66$ , not reaching its starting value.

Then a powerful electric motor is integrated into the circuit. The powerful electric motor consumed a current of 13 mA. But the voltage of the cell drops significantly to 1,1 V and the resting potential of the manganese dioxide electrode drops to  $-0,9$  V. All findings can be found in Figure 4.

**Interpretation:** With an integrated electric motor, the following electrochemical reactions take place:



Manganese is reduced from its oxidation state (IV) to (III) and the lithium ions produced are intercalated in the manganese dioxide structure. This reaction is not reversible like in the lithium-ion-accumulator.

### 3.2. The lithium-iodine-battery

The lithium-iodine-battery is a non-rechargeable battery, used in pacemakers for 50 years. Pacemakers need a relatively low current and there is a need for a battery with a low self-discharge in order to stay as long as possible in the body (e.g. Figure 5). The lithium-iodine-battery has all these prerequisites and can be described as a solid-state battery, because of the absence of a liquid electrolyte. Lithium iodide is the solid-state electrolyte in this battery, because of its capability to conduct lithium-ions. Metallic lithium is used as the anodic and polyvinyl pyridine as the cathodic material, in which the iodine is embedded [18,19]. Polyvinyl pyridine is toxic even when it comes into contact with the skin and is also very expensive. It seems unsuitable for use in chemistry classes. An alternative experimental setup for teaching is to build an electrode with activated carbon and iodine as shown below [20].

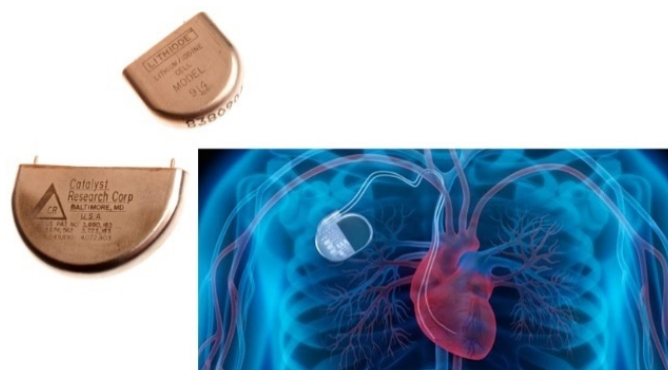


Figure 5. Representation of a pacemaker with a lithium-iodine-battery (source: Adobe Stock)



### 3.2.1. Experiment: lithium-iodine-battery

**Used equipment:** The same as in experiment 3.1.1, one additional pencil lead as collecting electrode with a diameter of  $\varnothing = 6.5$  mm (Faber-Castell Art.-Nr. TK9071), sieve shell with a diameter of  $\varnothing = 12$  mm and L = 85 mm (building's supplies store), modelling clay

**Used chemicals:** The same as in experiment 3.1.1, additionally: lithium iodide (GHS07), iodine (GHS08, GHS07, GHS09), activated carbon with a grain size of 1–3 mm

#### Preparation:

a) For manageability, a liquid electrolyte is used instead of a solid-state electrolyte. For this, 5 g of lithium iodide are dissolved in a mixture of 60 ml of dimethyl carbonate and 40 ml of propylene carbonate.

b) In this experiment a carbon-electrode according to OETKEN [12] is used. For this, a pencil lead is centered in a sieve shell, with 1–2 cm of the pencil lead, as the collecting electrode, standing out of the sieve shell. The sieve shell is filled with commercially available activated carbon and 2–3 iodine crystals. It is sealed on top with a little bit of modelling clay.

**Procedure:** A beaker is filled with approximately 75 mL electrolyte solution prepared as described in preparation. A piece of lithium wire with a length of approximately 3 cm is freed of its possible crust. The lithium oxide layer can be removed with a spatula or knife. The lithium metal should then be flattened with a spatula or knife for a larger electrode surface. It is held via a crocodile clip and put 2 cm into the solution. The carbon-electrode is then put inside the beaker. The complete experimental setup is described in Figure 6. At first the voltage without electrical load is measured and afterwards an electric motor is included into the circuit. The voltage and current are measured via the amperemeter and voltmeter. At the end, the voltage without electrical load is measured again. When required one can determine the potential of each half cell under electrical load and without electrical load.

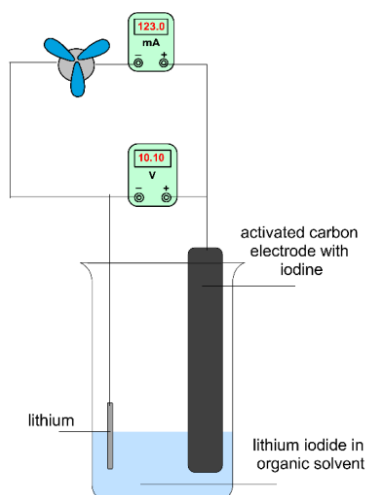


Figure 6. Experimental setup for the lithium-iodine-battery

**Results:** The voltage of the battery (without electrical load) increased to 3 V, the resting potential of the lithium

electrode is at  $-2,6$  V and the carbon-iodine electrode at  $+0,40$  V. After integration of the electric motor in the circuit the propeller is rotating very fast. The electric motor consumes a current of 6 mA. The voltage dropped to 2,34 V. The potential of the lithium-electrode remains stable at  $-2,27$  V whereas the potential of the carbon-iodine-electrode drops to 0 V. After a period of 10 minutes with a running motor, the voltage without electrical load is at 2,94 V. Then a powerful electric motor is integrated into the circuit. All findings can be found in Figure 7.

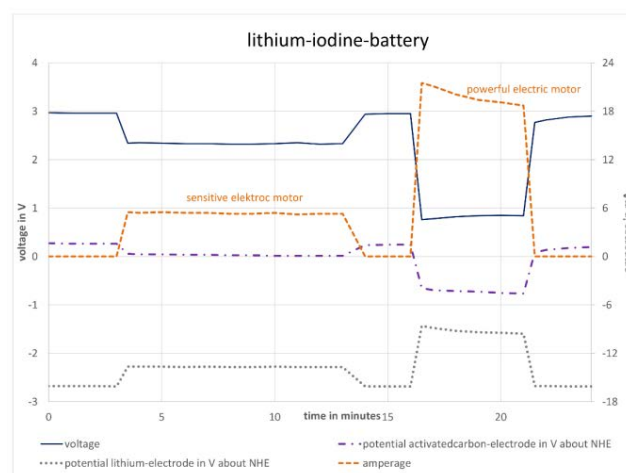
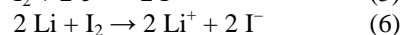
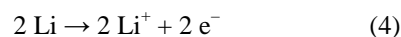


Figure 7. Measured voltage, current and potentials of the lithium-iodine-battery

**Interpretation:** With an integrated electric motor, the following electrochemical reactions take place:



Iodine is reduced to iodide and metallic lithium is oxidized to lithium cations. A reversal of this reaction is not possible in contrast to the lithium-ion-accumulator.

### 3.3. Lithium-Iron (II) Disulfide-Battery – a Rarity among Lithium-Batteries

The lithium-iron (II) disulfide-battery, or the lithium-pyrite-battery to be exact, is uncommon among the commercially available batteries. This battery has a voltage without electrical load of 1,8 V and a nominal voltage of 1,5 V. The nominal voltage is comparable to that of an alkaline zinc-manganese dioxide-battery, which is used instead of the lithium-pyrite-battery, because of a higher capacity and load voltage. Pyrite ( $\text{FeS}_2$ ) is a semiconductor like iron (II) sulfide ( $\text{FeS}$ ).

#### 3.3.1. Experiment: Lithium-pyrite-battery

**Used equipment:** The same as in experiment 3.1.1

**Used chemicals:** The same as in experiment 3.1.1, additionally: small blocks of pyrite of  $\varnothing = 35$  mm and L = 50 mm (Diameter and height not important for the experimental setup)

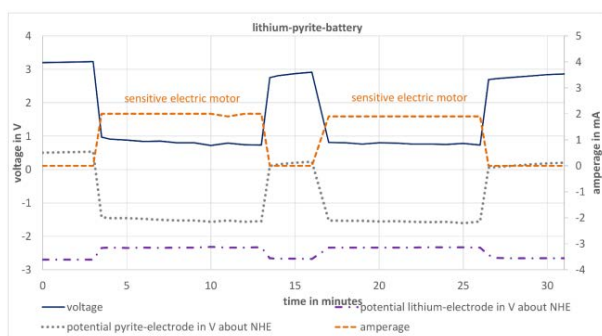
**Preparation:**

- a) For the electrolyte solution 10 g of lithium perchlorate are dissolved in a mixture of 60 ml of dimethyl carbonate and 40 ml propylene carbonate. For better solubility, the solution should be stirred with slight warming.

**Procedure:** In this experiment, a block of crystalline pyrite (e.g. Figure 8) was used instead of a powder. This can be seen as a disadvantage, on an electrochemical point of view, with the advantage to be able to see changes on the crystalline surfaces.



**Figure 8.** A crystalline block of pyrite



**Figure 9.** Measured voltage, current and potentials of the lithium-pyrite-battery

The experiment is conducted like experiment 3.1.1 and shown in Figure 3. Instead of the cone-shaped clay pot filled with the manganese dioxide mixture, a pyrite block is used that way, that a small portion of the block is above the solution in order to attach a crocodile clip as the positive pole.

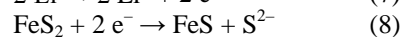
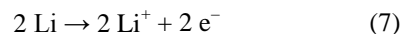
**Results:** The voltage of the battery (without electrical load) is at astonishing 3,5 V. The resting potential of the pyrite electrode is at +0,5 V and the lithium electrode is at around -2,7 V. After integration of an electric motor into the circuit, the propeller is rotating very fast. The electric motor consumed a current of 3,1 mA. The voltage dropped to 1 V. The potential of the pyrite-electrode drops to -1,6 V. After a period of 10 minutes with a running motor, the voltage without electrical load is at 2,8 V. The resting potential of the pyrite electrode is at 0 V. The measured values are comparable to a commercial lithium-pyrite-battery.

It can be assumed, that other unknown substances in the natural substance pyrite, which could decompose after the first integration of an electric motor, have an influence on

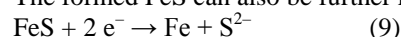
the potential. After the second integration of an electric motor, the measured potentials and voltage of the cell are as expected (e.g. Figure 9). The integration of a powerful electric motor was not successful.

The block of pyrite used in this experiment showed dark spots on the surface, which could stem from the formation of iron (II) sulfide or finely dispersed metallic iron.

**Interpretation:** With an integrated electric motor, the following electrochemical reactions take place:



The formed FeS can also be further reduced:



A lithium-pyrite-battery can also be realized with commercially available coarse pyrite powder.

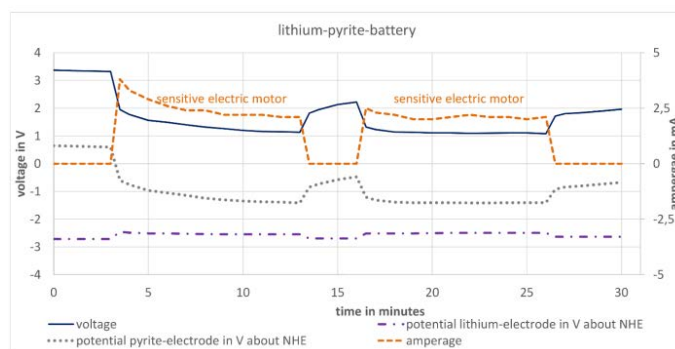
### 3.3.2. Experiment: Lithium-Pyrite-Battery with Coarse Pyrite Powder

**Used equipment:** The same as in experiment 3.1.1, one additional sieve shell with a diameter of  $\varnothing = 12$  mm and  $L = 85$  mm (building's supplies store), iron nail with  $L = 100$  mm, modelling clay

**Used chemicals:** The same as in experiment 3.1.1, additionally: coarse pyrite powder

**Preparation:**

- a) For the electrolyte solution 10 g of lithium perchlorate are dissolved in a mixture of 60 ml of dimethyl carbonate and 40 ml propylene carbonate. For better solubility, the solution should be stirred with slight warming.



**Figure 10.** Measured voltage, current and potentials of the lithium-pyrite-battery with the DIY-pyrite-electrode

**Procedure:** The iron nail is centered in a sieve shell as the collecting electrode. The sieve shell is then filled with coarse pyrite powder. It is sealed on top with a little bit of modelling clay. This DIY-pyrite-electrode is used in the experiment according to Figure 3, but instead of the clay pot, the DIY-pyrite-electrode is used.

**Results:** The results are similar to the results of experiment 3.3.1. Relatively high the voltage without electrical load can be traced back to impurities of the pyrite powder. A sensitive electric motor can be integrated into the circuit. After a period of 10 minutes, the voltage

without electrical load of the cell is comparable with that of a commercially available lithium-pyrite-battery. The resting potential of the pyrite electrode is at  $-0,9$  V. After a short break of three minutes, the battery can operate the sensitive electric motor (e.g. Figure 10). The integration of a powerful electric motor was not successful.

*Interpretation:* The occurring reactions are described in 3.3.1.

### 3.3. Interpretation of Battery Types

All four battery types presented can be easily integrated as experiments in laboratory trainings in higher education and upper secondary school. Despite the simple experimental setup, high voltages can be generated. Some battery assemblies require special materials, shown in Table 1. The lithium metal manganese dioxide battery and lithium metal iodide battery are common in everyday life. Their structure and how they work should be explained to pupils in the same way as that of the lithium-ion battery. In this article, simple experimental setups were presented.

However, the batteries are not rechargeable. That is why they are unusable for large-scale use as energy storage in the energy transition. The lithium metal pyrite battery is also suitable as a primary cell. Despite the sulfur compound, this is also not rechargeable and therefore unsuitable as an energy store. Oxygen-based lithium metal batteries seem to be better suited for this. The didactic processing of suitable experiments of the lithium metal-oxygen-battery has already taken place in [14].

Table 1. Comparison of battery types

battery type	system	voltage in volt	special features of the experimental setup
lithium-manganese dioxide battery	- metallic lithium - mixture of manganese dioxide and activated carbon	3,0-3,5 V	- special cone-shaped clay pot (flower watering)
lithium-iodine-battery	- metallic lithium - mixture of iodine crystals and activated carbon	3,0 V	- special electrolyte with lithium iodide in organic solvent
lithium-pyrite-battery (block of pyrite)	- metallic lithium - pyrite	3,5 V	- a block of crystalline pyrite (not easy to buy)
lithium-pyrite-battery (pyrite powder)	- metallic lithium - pyrite	3,5 V	- coarse pyrite powder (easy to buy)

## 4. Outlook

The lithium batteries and the corresponding experiments described so far, have found their particular application. The lithium-ion battery, on the other hand is used in various fields: device the automotive industry and as a energy storage used for solar and wind energy. In the applications, lithium-ion battery reaches its limits in these applications. Better results could be achieved with a lithium-oxygen battery,

which is currently the subject of intensive research nowadays. An experiment describing the lithium-oxygen-accumulator can be found here [14].

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