# Leclanché cell

Time required: 120 – 150 min + over night

## Aims of the experiment

- To construct a galvanic cell.
- To examine the Leclanché cell as a galvanic cell.
- To follow the path from galvanic cell to battery.
- The zinc-carbon battery and its characteristic curve.

## Principles

In 1780, the Italian researcher and physician *L. Galvani* noticed that a frog leg jerks when it comes into contact with iron and copper. He presumed that there was an electric effect at work. 20 years later, *A. Volta* developed the first battery (primary cell) in the form of the voltaic pile. Further developments in the "wet battery field" followed. However, none of these cells were suitable for everyday use since the electrolyte was in the form of a liquid. They are therefore not useful for mobile use for such things as pocket flash lights, mobile telephones, etc. Finally, in 1866 the first dry battery was patented, at that time still in wet form, by French physical chemist *G.* Leclanché. In the process, the electrolyte solution was turned into a gel using binders so that mobile use was possible.

The Leclanché cell has a (clamping) voltage of 1.5 V. The anode is made of zinc and the cathode is made of manganese dioxide and carbon. A thickened ammonium chloride solution is used as the electrolyte. Additionally, zinc chloride is used in order to increase the energy density (charging density) (see Fig. 2).


**Fig. 1**: Set-up and materials for the experiment.

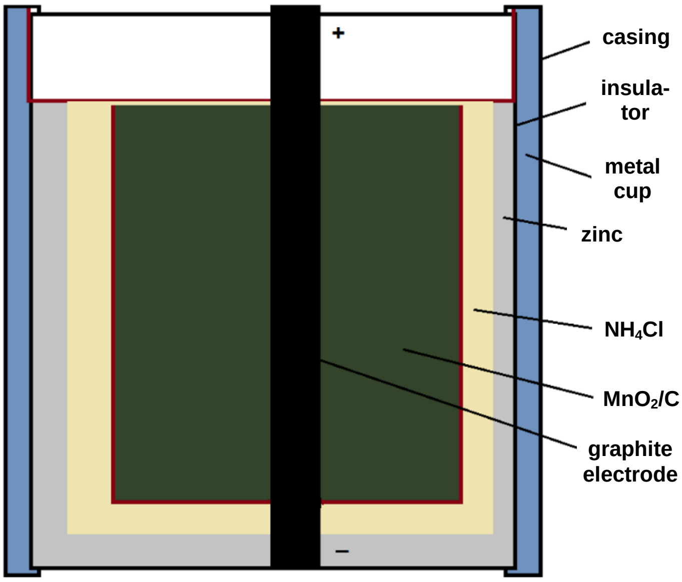


**Fig. 2**: Improved Leclanché cell: Cross section of a zinc manganese dioxide/carbon battery

What reaction is responsible for the current?

In a Leclanché cell many reactions are occurring in parallel. However, only some are relevant to the generation of current. The three most important are explained below.

At the anode, zinc is oxidised during discharge. At the cathode, manganese oxide is reduced. The overall equations are

Ox.: $Zn \rightarrow Zn^{2+} + 2\ e^-$

Red.: $2\ MnO_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ MnO(OH)$

The electrolyte solution reacts as follows.

$Zn^{2+} + 2\ NH_4^+ + 2\ Cl \rightarrow [Zn(NH_3)_2]Cl_2 + 2\ H^+$

In this experiment a Leclanché cell is constructed and compared to a zinc-carbon element. Also, a common zinc-carbon battery will be recreated and compared in the experiment.

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## Risk assessment

CAUTION: Zinc chloride is an environmental hazard and must not be discharged into the environment.

Zinc chloride, ammonium chloride and sodium hydroxide solution are corrosive or irritating. Wear goggles and a laboratory coat.

Manganese (IV) oxide is hazardous to health.

**Zinc chloride, dry**



**Signal word:**

**Hazard**

**Hazard warnings**

H302 Harmful if swallowed.

H314 Causes severe skin burns and severe eye damage.

H335 May cause respiratory irritation.

H410 Very toxic to aquatic life with long-lasting effects.

**Safety information**

P273 Avoid release into the environment.

P280 Wear protective gloves/protective clothing/eye protection/face protection.

P301 + P330 + P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.

P305+P351+P338 IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and if possible to do so. Continue rinsing.

P309+P310 IF exposed or you feel unwell: Immediately call a POISON CENTER or doctor/physician.

**Sodium hydroxide solution, dilute, approx. 2 N (8%)**

**Signal word:**

**Hazard**

**Hazard warnings**

H314 Causes severe skin burns and eye damage.

H290 May be corrosive to metals.

**Safety information**

P280 Wear protective gloves/protective clothing/eye protection.

P303+P361+P353 IF CONTACT WITH SKIN OCCURS (or hair): Remove/take off all contaminated, soaked clothing immediately. Rinse skin with water/shower.

P305+P351+P338 IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and if possible to do so. Continue rinsing.

P310 Call a POISON CENTER or doctor/physician immediately.

P301 + P330 + P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.

P406 Keep in corrosion-resistant containers with corrosion-resistant linings.

**Manganese (IV) oxide**


**Signal word:**

**Hazard**

**Hazard warnings**

H272 May intensify fire; oxidiser agent.

H302 Harmful if swallowed.

H332 Harmful if inhaled.

**Safety information**

P221 Avoid mixing with combustibles.

**Ammonium chloride**

**Signal word:**

**Caution**

**Hazard warnings**

H302 Harmful if swallowed.

H319 Causes serious eye irritation.

**Safety information**

P305+P351+P338 IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and if possible to do so. Continue rinsing.

## Equipment and chemicals

| | | |
|---|---|---|
| 1 | Electrochemistry demonstration unit, CPS | 664 4071 |
| 1 | Panel frame C50, two-level, for CPS | 666 425 |
| 1 | Electrochemistry table, CPS | 666 472 |
| 1 | Electrochemistry accessories set | 664 401 |
| 1 | Electrolysis cell | from 664 401 |
| 1 | Drip pan | from 664 401 |
| 6 | Paper diaphragm | from 664 401 |
| 2 | Crocodile clips | from 664 401 |
| 5 | Connecting leads | from 664 401 |
| 1 | Carbon electrodes | from 664 401 |
| 1 | Zinc electrodes | from 664 401 |
| 2 | Beaker, 600 ml | 664 132 |
| 3 | Beaker, 150 ml | 602 023 |
| 2 | Glass stirring rod | 665 217 |
| 1 | Scales | ADACB501 |
| 1 | Measuring cylinder, 100 ml | 665 754 |
| 1 | Measuring cylinder, 10 ml | 665 751 |
| 1 | Spatula, double ended | 604 5663 |
| 1 | Filter stand | 666 584 |
| 2 | Funnels, 150 mm | 602 671 |
| 1 | Folded filter, 110 mm, set of 100 | 609 081 |
| 1 | Zinc chloride, dry, 50 g | 675 5100 |
| 1 | Ammonium chloride, 100 g | 670 4000 |
| 1 | Manganese(IV) oxide, 100 g | 673 2200 |
| 1 | Graphite, 50 g | 672 1500 |
| 1 | Sodium hydroxide solution, dil, approx. 2 N | 673 8400 |
| 1 | Water, pure, 1 l | 675 3400 |
| 1 | Wash bottle, PE, 250 ml | 661 242 |
| 1 | Carboxymethylcellulose | 671 3820 |
| | Or: | |
| | Wallpaper paste, flour, corn starch, sauce thickener, etc. | |

## Set-up and preparation of the experiment

### Set-up of the experiment

Suspend the demonstration unit and the electrochemistry table in the panel frame. Place the drip pan in the centre of the electrochemistry table.

Fix the two half cells of the electrolysis cell with the screws so that a gap about 0.5 cm wide remains. In this gap, place two paper diaphragms one atop the other and screw the two half-cells tight. The electrolysis cell is now sealed. Now place a zinc and a carbon electrode into the second groove so that the electrode gap is very small (see Fig. 1).

### Preparation of the experiment

Construct two different cells. For the zinc-carbon cell without a depolariser, a 26% ammonium chloride solution is used. Transfer 39 grams of ammonium chloride to a beaker (150 ml). While stirring, add 111 ml of distilled water to this. The solution will suddenly become cold since the enthalpy of solution is being consumed.

For the Leclanché cell, prepare 40 ml of electrolyte solution. Place 10.4 g of ammonium chloride, 3.5 g of zinc chloride and 2 g of carboxylmethyl cellulose or methyl cellulose (wallpaper paste), flour, corn starch, sauce thickener, etc. into a beaker (150 ml) and mix well with a glass rod. Now, add 25 ml of distilled water while stirring. A highly viscous mass will form. Mix it well with the glass stirring rod.

To prepare a depolarisation mixture, add 20 g of manganese dioxide, 8 g of graphite, 4 g of ammonium chloride and 0.5 g of zinc chloride to a beaker (150 ml) and mix well with a glass stirring rod. Stir the mixture while adding 13 ml of distilled water (measure this with a measuring cylinder) to form a paste (see Fig. 3).

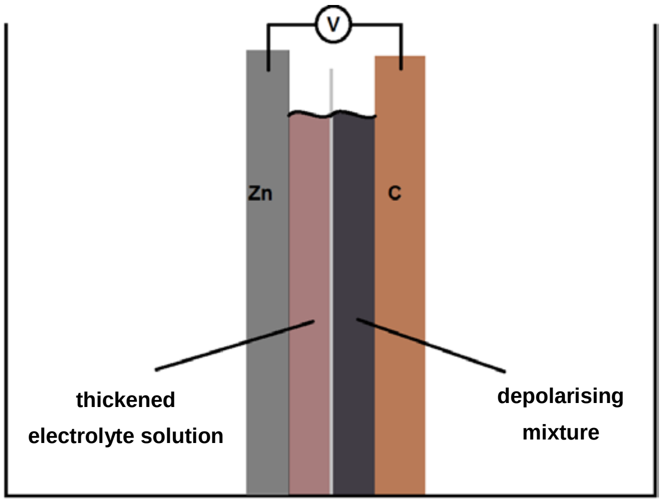


**Fig. 3**: Sketch of the equipment set-up.

Turn on the measurement of the external power source on the demonstration unit using the selector switch (6) (see Fig. 4). Connect the carbon electrode to the positive output socket (7) of the amperemeter. Connect the zinc electrode to the output socket (17) of the electric motor. Also connect the zinc electrode to the negative output socket (12) of the voltmeter. Connect the free outlet socket (17) of the electric motor to the negative outlet socket (7) of the amperemeter and the positive outlet socket (12) of the voltmeter (see Fig. 5). Set the rotating switch (15) to 2 V. Set the rotating switch (11) to 20 – 200 mA.

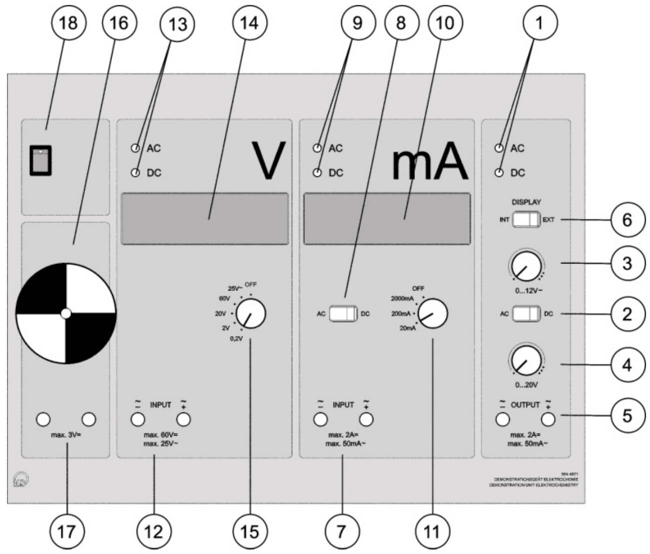


**Fig. 4:** Sketch of the demonstration unit.

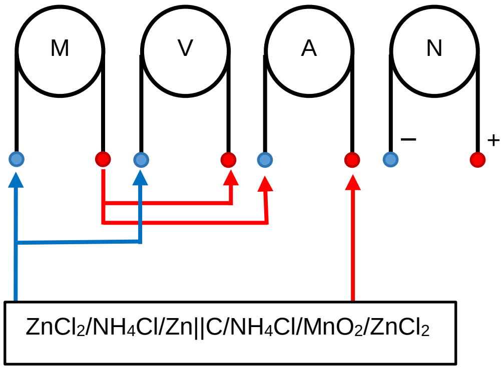


**Fig. 5:** Circuit for the experiment.

## Performing the experiment

### Zinc-carbon cell without depolariser

To investigate the zinc-carbon cell, both half cells of the electrolysis cell are filled with 26 % ammonium chloride solution. Divide the prepared solution into two equal fractions (about 75 ml). Turn on the demonstration unit using the switch (18). Observe the display and record the voltage and current every minute. After 15 minutes, the experiment can be ended. Collect the solution in a beaker (600 ml) and rinse the electrolysis cell and the electrode thoroughly with distilled water.

### Leclanché cell (fresh)

To investigate the improvement provided by Leclanché, the electrodes are re-used. In the anode space (zinc electrode), the thickened electrolyte paste is carefully filled in using a double spatula so that the diaphragm is not destroyed. In the cathode space (carbon electrode), the depolarisation paste is filled in carefully using a double spatula. Take care that the electrodes are pushed through to the bottom of the electrolysis cell. When the demonstration unit is turned on, the measurement restarts. Record the measurements (current and voltage) every minute. After about 20 minutes, the measurement can be ended. Transfer the electrolyte and depolarisation paste to a folded filter using the funnel and filter stand. Thoroughly rinse the electrolysis cell using tap water. Filter the rinsing water again. Rinse out the electrolysis cell again thoroughly with distilled water.

### Zinc-carbon battery

In order to simulate a commercially-available zinc-carbon battery, depolarisation paste and electrolyte solution are prepared again, transferred to the electrode spaces and allowed to sit for at least 18 hours. In the process, the excess liquid will dry. Start the measurement again the next day and observe for a duration of 30 min. Record the measurements (current and voltage) every minute.

## Observation

In all cases, the electric motor starts. In the first case without the depolarisation mixture, the measurements decrease very rapidly. The freshly-prepared Leclanché cell provides better results. The dried Leclanché cell also has a longer lifespan and can therefore better maintain current and voltage.

## Evaluation

The following tables contain the measurements from the experiment.

**Tab. 1:** Measurement results from the zinc-carbon element without depolarisation paste, the freshly-prepared Leclanché cell and the dried Leclanché cell (the battery).

| t | zinc/carbon | | Leclanché fresh | | battery | |
|---|---|---|---|---|---|---|
| | U (V) | I (mA) | U (V) | I (mA) | U (V) | I (mA) |
| 0 | 980 | 9.4 | 1068 | 12.1 | 1250 | 15.9 |
| 1 | 730 | 8.8 | 982 | 11.4 | 1110 | 15.2 |
| 2 | 580 | 8 | 899 | 10.9 | 1099 | 14.7 |
| 3 | 508 | 7.3 | 852 | 10.1 | 1065 | 13.9 |
| 4 | 460 | 7.1 | 807 | 9.8 | 982 | 12.7 |
| 5 | 427 | 6.9 | 778 | 9.4 | 912 | 11.1 |
| 6 | 401 | 6.9 | 758 | 9.2 | 806 | 10.4 |
| 7 | 380 | 6.8 | 742 | 8.9 | 771 | 9.9 |
| 8 | 364 | 6.8 | 730 | 8.8 | 739 | 9.6 |
| 9 | 352 | 6.6 | 718 | 8.6 | 710 | 9.1 |
| 10 | 346 | 6.6 | 708 | 8.5 | 689 | 8.8 |
| 11 | 331 | 6.8 | 700 | 8.5 | 673 | 8.7 |
| 12 | 319 | 7.1 | 692 | 8.4 | 662 | 8.5 |
| 13 | 277 | 7.9 | 684 | 8.3 | 653 | 8.3 |
| 14 | 252 | 7.7 | 679 | 8.3 | 646 | 8.3 |
| 15 | 249 | 7.7 | 669 | 8.2 | 640 | 8.2 |
| 16 | | | 662 | 8.1 | 636 | 8.1 |
| 17 | | | 659 | 8 | 631 | 8.1 |
| 18 | | | 653 | 8 | 628 | 8 |
| 19 | | | 649 | 8 | 625 | 7.9 |
| 20 | | | | | 621 | 7.9 |
| 21 | | | | | 618 | 7.8 |
| 22 | | | | | 614 | 7.7 |
| 23 | | | | | 612 | 7.7 |
| 24 | | | | | 610 | 7.7 |
| 25 | | | | | 608 | 7.7 |
| 26 | | | | | 605 | 7.7 |
| 27 | | | | | 603 | 7.7 |
| 28 | | | | | 602 | 7.6 |
| 29 | | | | | 600 | 7.6 |
| 30 | | | | | 598 | 7.6 |
| 31 | | | | | | |

From the graphical plot, characteristic curves of the cell can be obtained. In the process, the voltage and the current are plotted against time. Figure 6 contains the graphical plot of the zinc-carbon cell without the depolariser.

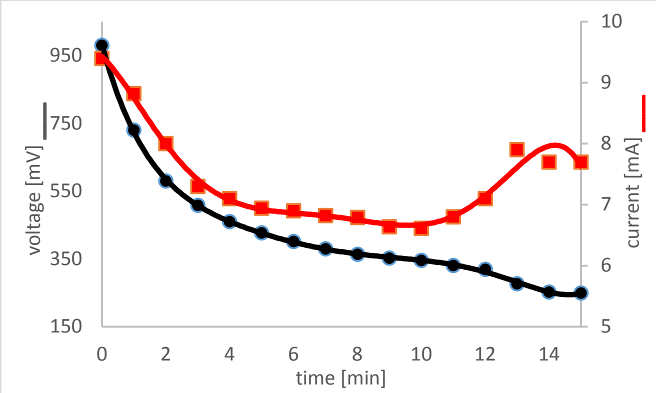


**Fig. 4**: Characteristic curves of the zinc-carbon cell without depolarisation paste.

For the measurement of the freshly-prepared Leclanché cell, the following graphical representation (Fig. 7) of the characteristic curve was obtained.

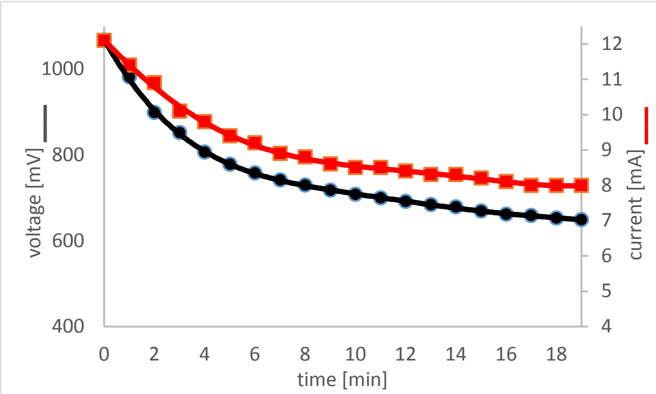


**Fig. 5**: Characteristic curves from the freshly-prepared Leclanché cell.

For the measurement of the battery, the following graphical relationship (Fig. 8) of the characteristic curve was obtained.

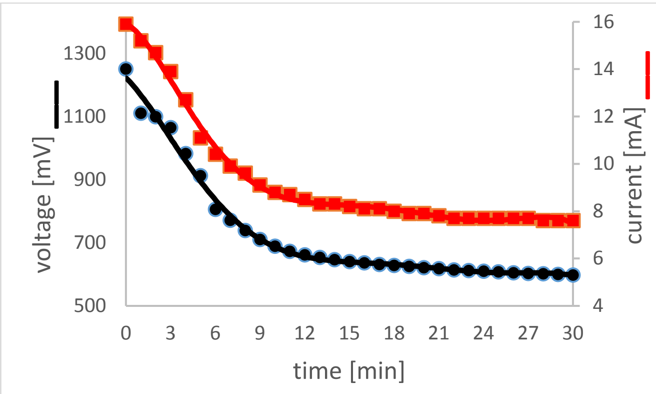


**Fig. 6**: Characteristic curves from the battery (dried Leclanché element).

## Results

The characteristic curves reflect the characteristic discharging processes of primary and secondary cells (batteries and accumulators). The Leclanché cell is still very applicable today in the dried and modified version in the battery industry (as zinc-carbon batteries).

The results of the Leclanché cell are much better than those of the zinc/carbon cell without a depolariser. The explanation for this is as follows. In both cases, zinc goes into solution at the cathode. In the simple variant without the depolariser, however, hydrogen is generated at the anode

$$2\ H_3O^+ + 2\ e^- \rightleftharpoons 2\ H_2O + H_2$$

which becomes bound to the adsorptive surface of the electrode. The approach of the electrolyte to the carbon electrode is prevented as a result, and a polarisation takes place, along with a strong drop in power output.

On the other hand, in the Leclanché cell the hydrogen generation is suppressed by the manganese dioxide in the depolarisation mixture.

$$2\ MnO_2 + 2H_3O^+ + 2\ e^- \rightleftharpoons 2\ MnO(OH) + 2\ H_2O$$

There are other processes that occur in a Leclanché cell that are much more complicated. Various kinds of zinc salts form.

## Ongoing evaluation

There are other load curves that can be recorded from the self-prepared Leclanché cell. These can be investigated practically using commercially available batteries. For comparisons, see Experiment C4.4.4.7a.

## Cleaning and disposal

Add sodium hydroxide solution to the ammonium chloride solution.

*CAUTION! Only perform in the fume hood, ammonia will be released.*

$$NH_4Cl + NaOH \rightarrow NH_3\uparrow + H_2O + NaCl$$

The ammoniacal solution is tested for pH. If it is too basic, (11 or higher), the solution must be neutralised with dilute acid. Finally the solution can be disposed of down the laboratory drain with plenty of water. The rest of the pastes are added to a folded filter using the funnel and filter stand (it is more practical to dispose of the depolarisation paste in one filter and the electrolysis paste in a second filter). Thoroughly rinse the electrolysis cell with tap water and add the solution to the filter. Then, thoroughly rinse the electrolysis cell with distilled water and dry. Rinse the electrodes well. Polish the zinc electrode with the grindstone.

Rinse the pastes in the filter with dilute sodium hydroxide solution.

*CAUTION! Only perform in the fume hood. Ammonia will be released*

This converts the excess zinc salts to insoluble zinc hydroxide. Filter the mother liquor again. Dry the filters overnight in the fume hood; they can then be disposed of in the waste container for inorganic solids. The filtered mother liquor can be disposed of in the laboratory drain.