Teachers' Card

Index

Index 1

General Introduction 2

Extended background information 2

Learning Outcomes 5

Key Competence European Framework 5

United Nations' Sustainable Development Goals 6

Lab Procedure 7

Learning Pathway 10

Evaluation 10

Acknowledgement..10

Sources..11

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General Introduction

The present toolkit will introduce students to the metallic packaging issues, suggesting four easy experiments that show:

1. a physical method to select two different metals used in the food packaging (Aluminum and steel);
2. a chemical method to select the same metals;
3. the reduction potential series, the concept of corrosion, anodic protection and passivation;
4. the electrochemical deposition of metals (galvanoplastics), in particular Tin (one of the first components of food disposable metallic packaging).

Key words:

Metal recycling, redox reactions, electrochemistry

Extended background information

This toolkit introduces the students to the subject of metallic packaging recycling, the so-called "tin can" that started with the boxes in tinplate that were made by rolling and soldering to a small cylinder a band of metallic sheet, covered by a thin layer of tin on the side in contact with food to protect the metal from corrosion. The small cylinder was then capped with two metallic discs tightly fold over its edge. The can-opener was the essential tool to open this kind of packaging and was included in the kitchen, camping and soldier tools. In fact, the food storage in metallic boxes seems to be developed to warrant to Napoleon's army an effective system for storing foodstuffs.

Today, almost all the metallic package are produced by pressure deformation of Aluminium or stainless steel discs tightly capped on one side by a disc made by the same metal and generally equipped with a ring for tear opening.

Iron and steel

Iron (Fe) is the fourth most abundant on the Earth crust representing its 5%, it probably compose the 16% of the whole Earth mass and it is rather abundant in the Universe. It is so frequent because it is the result of the nuclear fusion in the large stars.

Pure Fe is used in few applications such as the core of the voltage transformers, but it is commonly used in alloy with Carbon or other metals. Fe production needs coke that is one of the strategic materials for the EU economy.

Aluminium

Aluminium (Al) is the element whose atomic number is 13 and it's in the third period, third group of the current element's periodic system.

Because of its relative abundance equal to 8% it is the third most abundant element on the Earth's crust after oxygen and silicon. In nature, it is present almost exclusively as the stable isotope ^{27}Al, always oxidized, and in form of feldspars, mica, clays and kaolins. The pure oxide is named Corundum of which some varieties are known as Ruby and Sapphire.

The hydrated oxide (Bauxite) is used for the metal extraction. Because of the low standard reduction potential (E^0= -1.66V), it isn't possible to get the metal from high temperature reduction with coke, as for Iron and Copper, but it is necessary to provide for an electrochemical process, as for Magnesium and Titanium.

In the Hall-Herould process (1886), Bauxite is melted at 1000 °C with Cryolite ($3NaF \cdot AlF_3$). This latter has been recently replaced with artificial mixtures of Sodium fluorides, Aluminum and Calcium. The reduction happens at the base of the electrolytic cell over coal anodes with an energy requirement that today is circa 14 Kwh per 1 Kg of Al[i], in accordance with the cell reaction:

$$2Al_2O_3 + 2C \longrightarrow 4Al + 3CO_2$$

The melted metal comes out of it (fusion point: 660 °C) with a title of 99.4-99.9%. Alcoa has recently introduced a preventive conversion to Al carbide and Calsmelt has reduced the operating temperatures adding Aluminum wreckage into the blend of melted minerals, lowering the energy consumption.

In 2017, Al world production was about 63.4 million tonnes, of which 57% was produced in China and just 12% in Europe, with an absorption of about 3.5% of the world electric production. The high cost of energy, together with the reduction of the internal request and the increase of recycling, is the reason why, in the last years, Italy, the Netherlands, and the United Kingdom have abandoned the production of primary Aluminium[ii]. In the EU in 2012, just slightly over 2 million tonnes of Bauxite were mined, produced solely in Greece, France, and Hungary, while the production of Alumina, mainly used in refractory materials, reached 5.6 million tonnes. The European Aluminium production also suffers the Calcium fluoride's uncertainty procurement, that the EU imports for 70%, mostly from the Popular Republic of China, responsible of 2/3 of the world extraction[iii].

Al is one of the the mostly used metal, second only to Iron, thanks to his low density (2690 kg m^{-3} at 20 °C) and the corrosion resistance due to the natural formation of a protective layer from the reaction with Oxygen (a process known as passivation). Thanks to the relatively low fusion point, Al can be processed via die-casting or hydroforming. Light alloys based on Al, Magnesium, Copper and Zinc depending on the use, are employed in aviation, but also for boat's hulls and sports cars' details. The passivation layer can be thickened with the so-called anodization process that allows also a tenacius colouration: for this reason, Al is largely used for the realization of frames in buildings.

Because of its good electric conductibility, Al (whether in its pure form or as a metal alloy with Magnesium and Silicon to increase the breaking load) replaces Copper in overhead electrical lines, as it allows the production of cables which weigh less on the support pylons. Because of its good thermal conductibility, it is used in heat exchangers, and Aluminium-Silicon-Copper alloys are used to create engine parts[iv].

The versatility of this metal and its alloys has given engineers and stylists a large design liberty for creating a lot of objects for professional, sports and domestic uses. Al is largely used for packaging, to the extent that the EU has set Al recycling goals of at least 50 % by 2025, and 65 % by 2030[v].
In ord0er to recycle Al, it is sufficient to separate it from other wastes, to pre-treat it at a temperature of 500 °C to burn varnishes and labels, to melt it again at a temperature of 800 °C in an inert atmosphere, impurity removal, and to pour it into bars or plates. The yield on the starting waste is equal to 87 % but the saving of energy -and of relative CO_2 emissions - that would be consumed for the production of primary Al from minerals is equal to 95%[vi].

In the packaging sector, small amounts of Al are adhered to thin sheets or sprayed on different materials (cardboard or plastic) to block the entrance of Oxygen and to allow a longer duration of the stored food under inert conditions. However, the recovery from these polylaminate films is exceptionally difficult.

In the human body, Al is present at concentrations below one part per million and, in comparison with the relative abundance, it stands above only Silicon in the elements' ranking on which *Homo Sapiens* seems to have evolved on. In general it seems that Al is neither essential to living beings nor particularly toxic, despite the high concentration in the lithosphere and the complex geochemical cycles that force continuous contacts with the biosphere. But, even if the slow evolution of life remained almost indifferent to Al, humankind, in his relatively short story, has wisely used Al minerals at the beginning and then, starting from 1900s and as a result of its strategic value in aeronautics, has massively introduced this metal in his technological paraphernalia, making Al one of the materials on which the surge of our development in the last decades is based[vii].

Al dusts violently react with Oxygen, for this reason they are used in the explosives industry. The latter's workers, as those involved in the production of primary and secondary Al, and those using

Teachers' Card

Alumina powders to produce refractories, are exposed to the risk of contracting Pneumoconiosis, a respiratory system's pathology that can be associated to pulmonary fibrosis and emphysema.
It seems that Al compounds are not absorbed into our digestive system. Indeed they make up medicaments to treat stomach acid and Aluminium PolyChloride is used as flocculant also in drinking water treatment plants.

Learning Outcomes

By the end of the lesson the students will be able to:

- Act in a chemistry laboratory with increasing confidence
- Recognize the typical metals used in packaging

Key Competence European Framework

Literacy competence
S1. Ability to understand and interpret concepts, feelings, facts or opinions in oral and written form.
S2. Ability to express concepts, feelings, facts or opinion in written and oral form.
S3. Ability to interpret the world and relate to others.
Multilingual competence
S1. Ability to understand and interpret concepts, feelings, facts or opinions in oral and written form.
S2. Ability to express concepts, feelings, facts or opinion in oral and written form.
S3. Ability to interpret the world and relate to others.
S4. Ability to interact in an appropriate and creative way in any situation.
S5. Knowledge of vocabulary, grammar and language.
S6. Appreciation of cultural diversity.
S7. Ability to use technical language accordingly to the field of work.
Mathematical competence and competence in science, technology and engineering
S1. Ability to use constructed thinking in order to solve a problem in every situation.
S2. Understanding of mathematical term and concept and know how to apply it.
S3. Ability to model mathematically a situation from the real world and to transfer mathematical expertise to non mathematical contexts.
S4. Readiness to address new problems from new areas.
S5. Capacity for quantitative thinking.

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S6. Ability to extract qualitative information from quantitative data
S7. Ability to formulate problems mathematically and in symbolic form so as to facilitate their analysis and solution.
S8. Ability to design experimental and observational studies and analyse data resulting from them.
S9. Ability to formulate complex problems of optimisation and decision making and to interpret the solutions in the original contexts of the problems
Citizen competence
S1. Ability to effective interaction with other people
S3. Ability to work effectively and collaborate with other team members

United Nations' Sustainable Development Goals

The Sustainable Development Goals are the blueprint to achieve a better and more sustainable future for all. They address the global challenges we face, including those related to poverty, inequality, climate change, environmental degradation, peace and justice.

	1 No poverty; 2 Zero hunger — Enable access to basic services		10 Reduced inequalities — Equal access to global expertise
	3 Good health and well-being — Safe medical devices		11 Sustainable cities and communities — Sustainable urbanization
	4 Quality education — Access to education	✓	12 Responsible consumption and production — Responsible consumption and production
	5 Gender equality — Less hardship, more opportunities		13 Climate action — Strengthen resilience, reduce disaster impact
	6 Clean water and sanitation — Safe and affordable water		14 Life below water — Reduce marine pollution
	7 Affordable and clean energy — Energy – the golden thread		15 Life on land — Sustainable use of terrestrial ecosystems

	8 DECENT WORK AND ECONOMIC GROWTH Safety of workers and economic growth		16 PEACE, JUSTICE AND STRONG INSTITUTIONS Promote peaceful and inclusive societies
	9 INDUSTRY, INNOVATION AND INFRASTRUCTURE Resilient infrastructure and sustainable industrialization		17 PARTNERSHIPS FOR THE GOALS Better access to technology and innovation

Lab Procedure

This activityis composed by a series of four experiments. The first couple can be easily done by with instruments easy to find. The third one and the fourth one need Tin slats and Zinc granules that are not available everywhere.

Experiment 1

Necessities

- a large magnet (i. e. you can bring it from broken woofer or bike dynamo);
- some tin can made by Aluminium (Al);
- some tin can made by steel.
- sturdy scissors (i.e. that for electrician)

Cut the tin cans made by different materials and mix the pieces together. Use the magnet to separate them. Since steel is mainly made by iron, it is attracted by the magnet meanwhile Aluminium does not. This is how you can use physical properties of Aluminium and steel to tell apart different type of tin cans.

Experiment 2

Necessities

- safety gloves and glasses;
- solid NaOH (it is possible to find it in some shops, it is used to gush out siphons);
- a teaspoon;
- a funnel;

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- some test tubes
- a test tube stand;
- a stirring bar;
- hot water.

Wear safety glasses and gloves. Put half of the teaspoon in the clamped test tube using the funnel. Fill about one third of the test tube with the hot water. Heating water beforehand halps to speed up the dissolution of NaOH. The solution should be mixed by using the stirring rod until all the NaOH is dissolved. Then put carefully a piece of steel can into the test tube. In NaOH, first the protective Sn layer that protect steel will react with the strong base forming $Na_2[Sn(OH)_6]$, thus the formation of few bubbles of gas may be observed.

$2\ NaOH + Sn + 4\ H_2O \rightarrow Na_2[Sn(OH)_6] + 2\ H_2\uparrow$

Since steel itself does not react with NaOH, nothing more should be observed.

Then, a piece of Aluminium could be carefully put into the same test tube or in another containing the same solution. Aluminium violently reacts with NaOH forming sodium aluminate:

$2\ NaOH + 2\ Al + 6\ H_2O \rightarrow 2\ Na[Al(OH)_4] + 3\ H_2\uparrow$

You have used chemical properties of steel and Aluminium to differentiate tin cans with different compositions.

Experiment 3

Necessity

- 50 mL beker;
- $SnCl_2$ powder (may be replaced by $Sn(NO_3)_2$, in this case you won't need to add HCl);
- HCl solution;
- water;
- Zinc granules.
- Petri's dish.

About half of a teaspoon of $SnCl_2$ should be dissolved in 50 mL of water. In dilute solution $SnCl_2$ Hydrolysis occurs forming an insoluble compound:

$SnCl_2\ (aq) + H_2O(l) \rightarrow Sn(OH)Cl\ (s) + HCl\ (aq)$

A few drops of HCl solution need to be added to move the equilibrium to the left, to avoid that the solution becams cloudy and better the visibility of the following reacton with the metal.The addition of acid also prevent the formation of precipitates by removing the carbonate ions from the water.

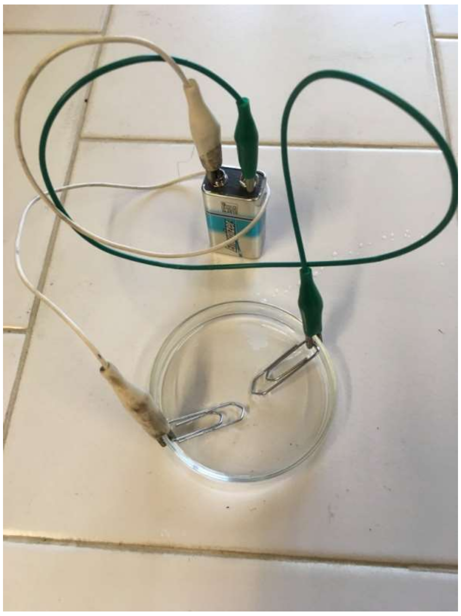
Fill 3/4 of the Petri dish with the solution and store it for the experiment 4.

Place some Zn granules in the ramaning solution in the beker, after some time the Zn granules will be coverde by a black a dusty layer of Sn. The following reaction occurs because Zn is more reactive than Sn:

Zn (s) + $SnCl_2$ (aq) → $ZnCl_2$ (aqu) + Sn (s)

A similar reaction is used in the production of tin cans to cover steel with a protective layer of Sn.

Experiment 4



Necessities

- a 9V battery;
- two paper clips;
- two electric cables, 10 or 20 cm long, with two crocodile connectors each one.

The solution in the Petri's dish, stored during experiment 3, will be used to perform an electrodeposition experiment. Clamp the paper pins to the Petri's dish edge by using one crocodile clip of each cable (see figure below). Connect the other crocodile clip of each cable to the two poles of the 9V battery. Keep the test apparatus veri still for best results and wait for few minutes. The formation of a metallic web from one paperclip should be observed.

The electric current from the battery induce a non-spontaneous reaction of $SnCl_2$ solution. Sn is reduced to the paperclip connected to the negative pole of the battery (cathode), while Cl_2 gas is formed near that connected to the positive pole of the battery (anode).

$SnCl_2$ (aq) → Cl_2 (g) + Sn (s) $\quad \Delta V$

Electrochemical reduction is used to obtine pure Aluminium from fuesed ores and consume about the 3% of all Word's electric energy. Due to this is much more energy efficient to recycle old Alluminium cans than produce them from the metal contined into ores.

Electrodeposition can be used to cover steel with Sn as well. Thin cans are coverd by Sn simiilarly to the paperclip connected to the negative pole of the battery.

<u>After this workshop it is recomanded to ventilate the room becouse of the different gasses formed during the experiments.</u>

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Learning Pathway

Step 1- Time & Activity: 15 minutes - Teacher do a short introduction with the halp of the tutorial video.

***Step 2 – Time& Activity**:* 90 minutes- Students are divided into groups (preferably the number of students in one group is 2 or 3). Each group performs the sequence of experiments.

Evaluation

Questions

1. What materials compose the metal package for food?
2. Which are the three main advantage in recycling Aluminum?
3. ......

Answers

1. Tin can are made by:
   1.1. tinplate (a steel band covered by a thin layer of tin);
   1.2. Aluminium;
   1.3. stainless steel.
2. The three main advantage in recycling Aluminium are:
   2.1. to save the 95% of the energy used to produce it from the mineral (14 kWh/kg^{-1} of Al);
   2.2. to reduce the amount of wastes that go to the landfill, in fact Al even if send to the 2.3. incinerator, do not reduce its volume;
   2.3. to mitigate the landscape impact of the mines reducing the water and chemicals consumption (es. fluorspat) and the environmental impact of the mining slag.

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