



L'eredità di Alessandro Volta: le pile dal 1800 a oggi

Luigi Fabbrizzi
Dipartimento di Chimica
Università di Pavia

Scuola Segre 2022 - "XIV edizione 16 - 25 novembre 2022"



DOVE E QUANDO
E' NATA LA
PRIMA PILA?



Wilhelm König, Ein Galvanisches Element aus der Partherzeit? *Forschungen und Fortschritte* 1938, 14, 8–9

La pila di Baghdad – ~200 a.C.

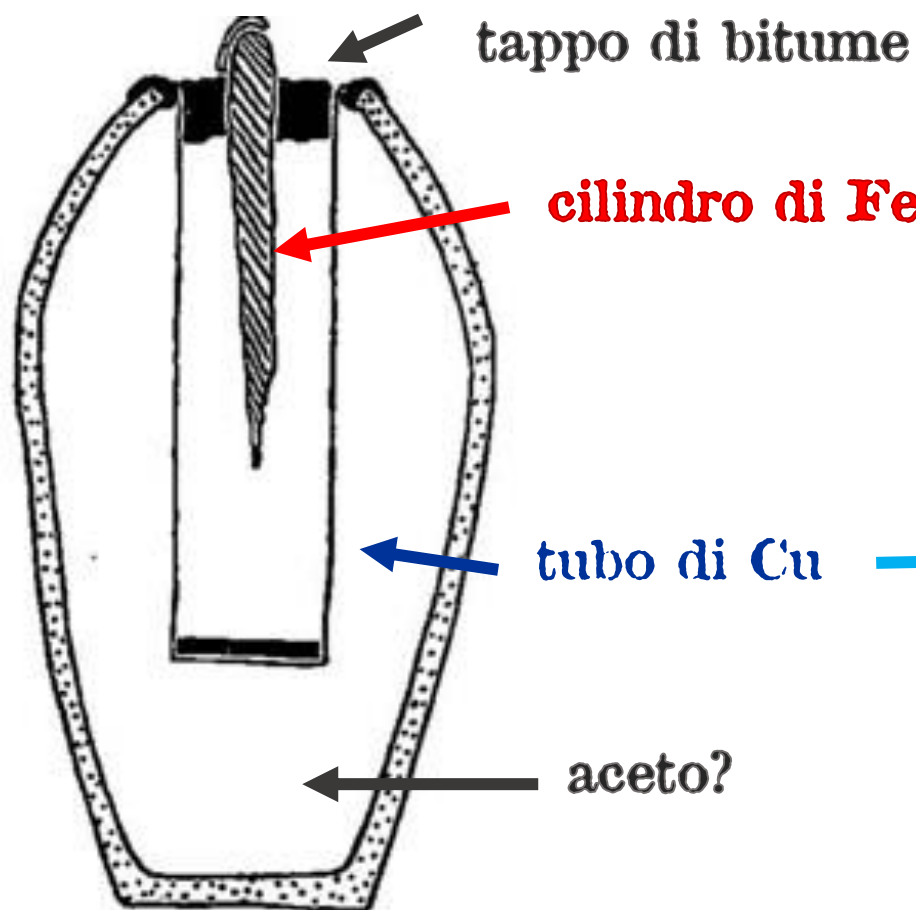


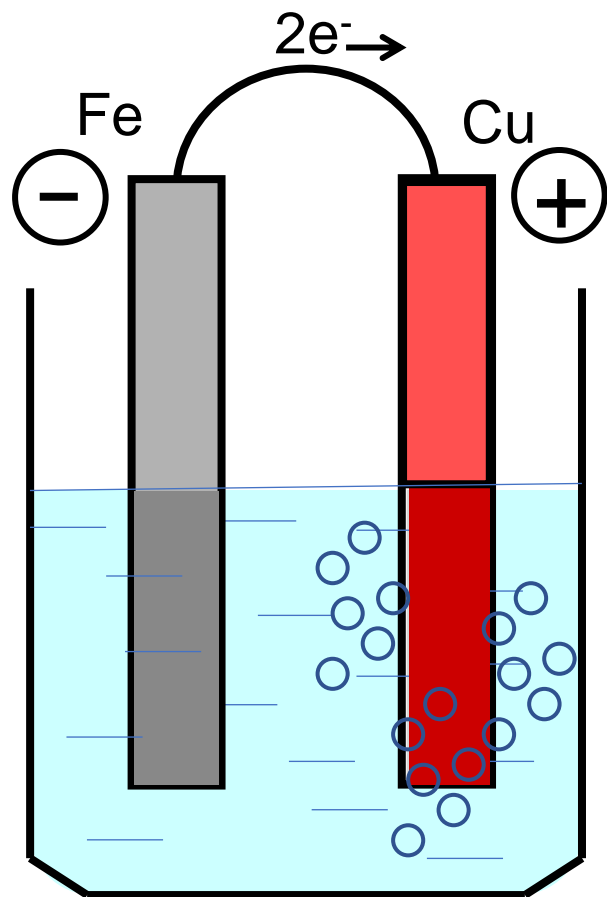
Abb. 2. Schnitt durch das Element



$$\Delta E^\circ = 0.44 \text{ V}$$

$$\Delta E^\circ = \sim 0.5 \text{ V}$$

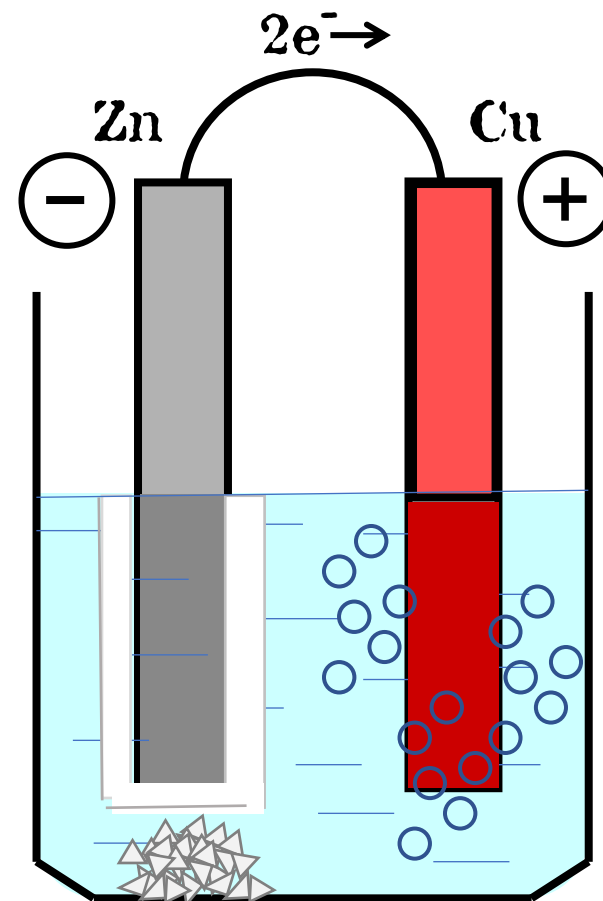




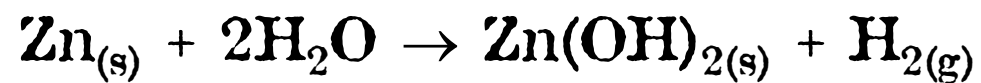
↑
 $\text{CH}_3\text{COOH}_{(\text{aq})}$



Pila di Baghdad



↑
 $\text{NaCl}_{(\text{aq})}$



Pila di Volta

Cronologia delle 'pile'

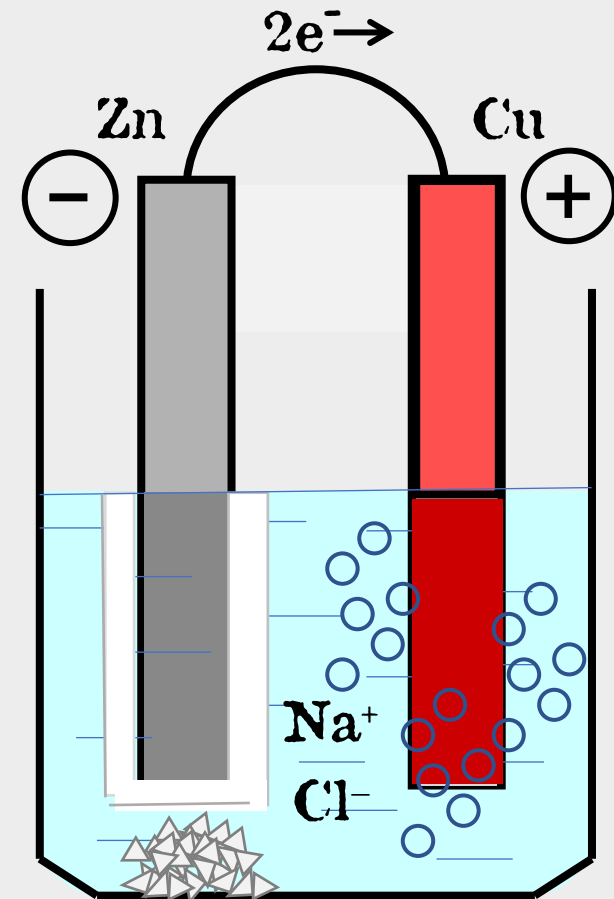
Volta - 1800

1800 1820 1840 1860 1880 1900 1920 1940 1960 1980 2000



La pila di Volta (1799)
(versione Rame/Zinco) in
esposizione presso il Tempio
Voltiano, Como

I difetti della pila di Volta



- ☐ Si forma Zn(OH)_2 sull'elettrodo di Zn
- ☐ H_2 viene adsorbito sull'elettrodo inerte (Ag, Cu)

⇒ aumenta la resistenza della cella, diminuisce l'intensità di corrente

William Cruickshank (1740-1811)
Royal Military Academy, Woolwich

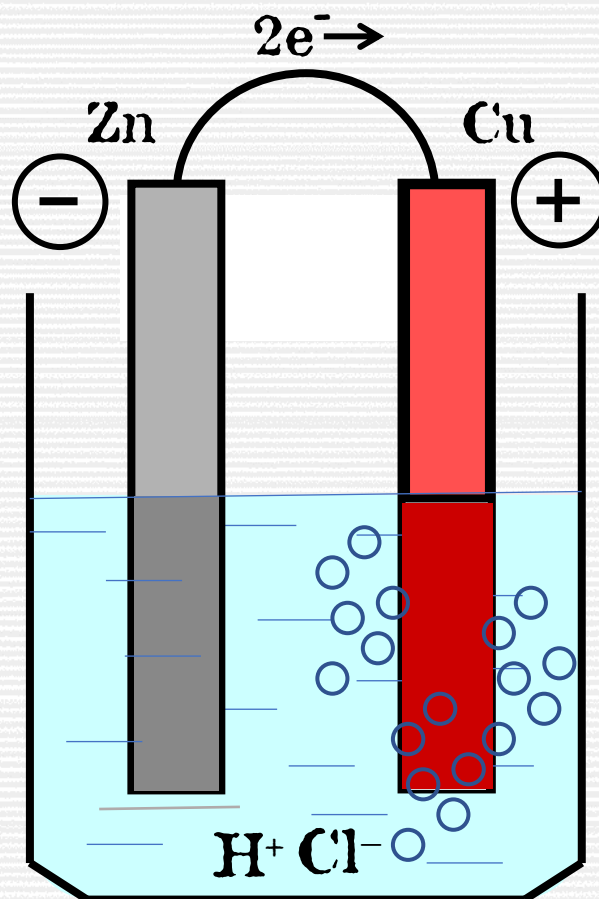
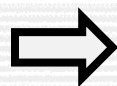


usano come elettrolita
 NH_4Cl o HCl

Humphry Davy (1778-1829)
Royal Institution of England, London

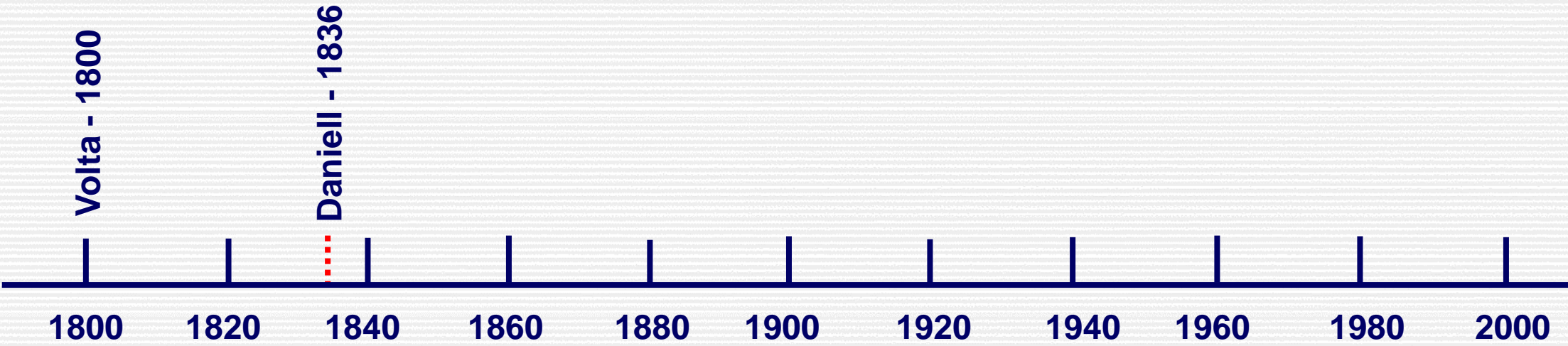


acido forte



non si forma
 $\text{Zn}(\text{OH})_2$

Cronologia delle 'pile'





John Frederic Daniell
(1790-1845)

Profesor of Chemistry
East India Company's Military
Seminary at Addiscombe, Surrey

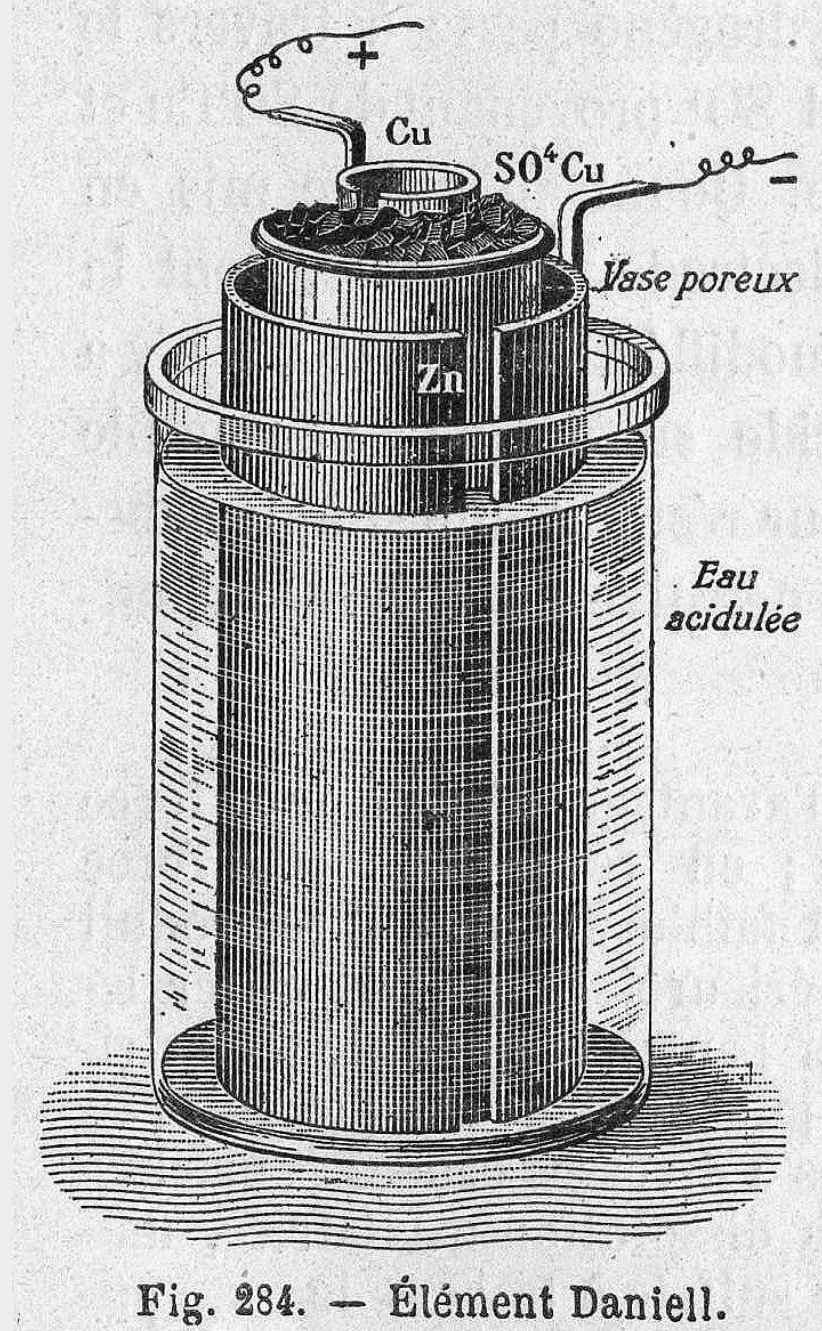
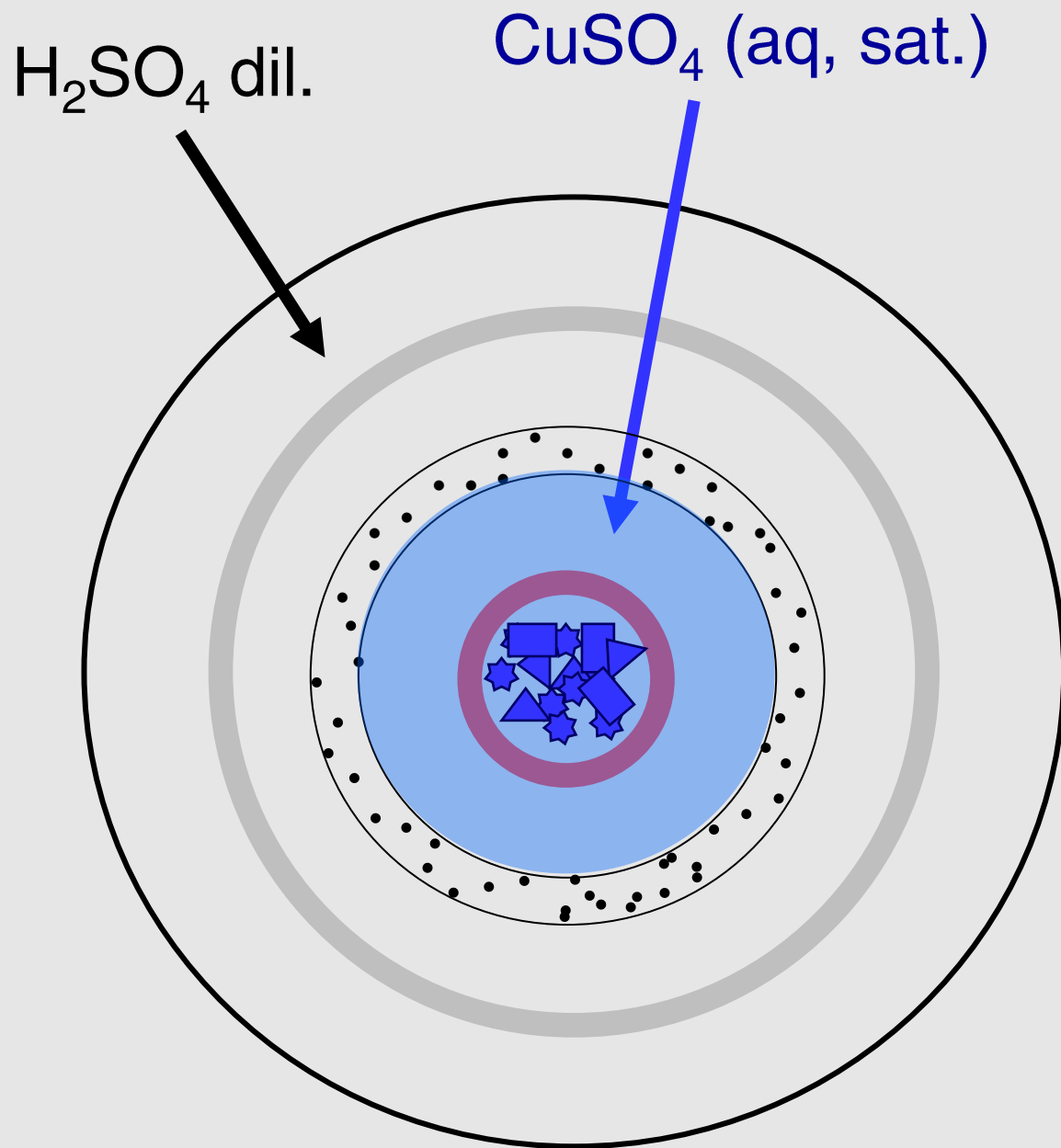


Fig. 284. — Élément Daniell.

La cella Daniell (1836)
Gillard - *Leçons de Physique*, Éditions
Vuibert et Nony, Paris, 1904



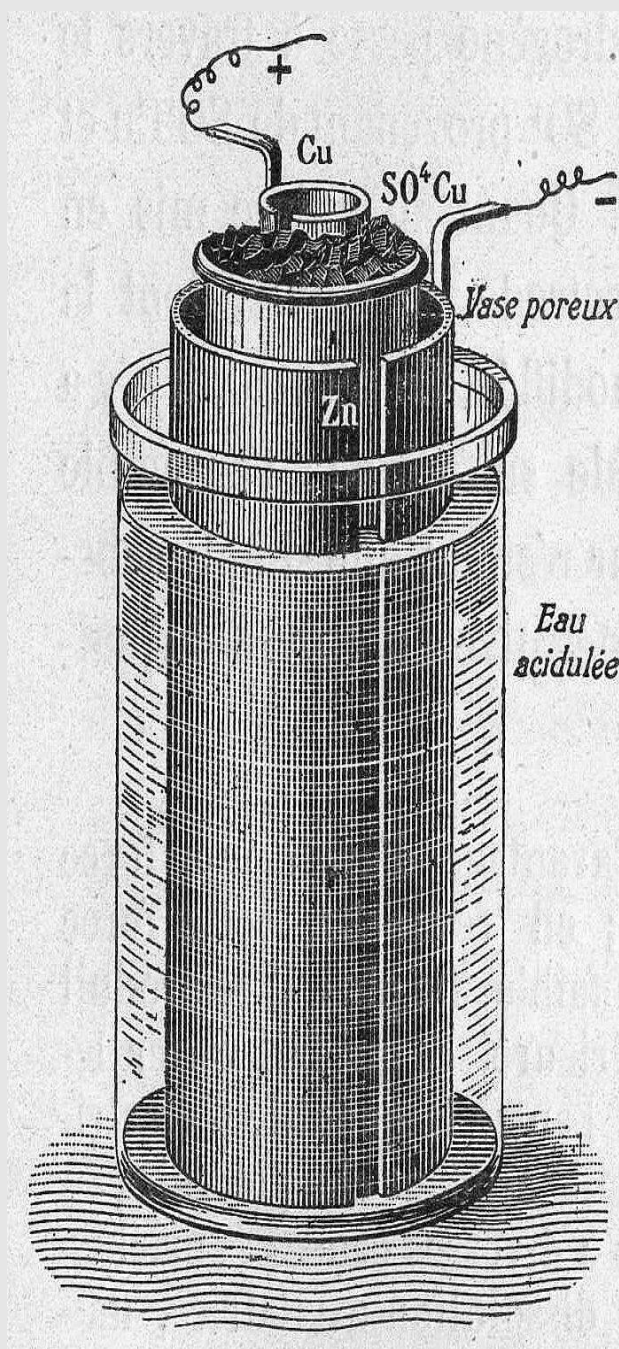
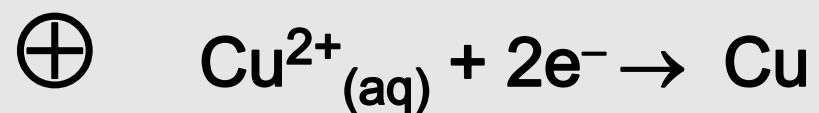
**vaso di
vetro**

**cilindro
di zinco**

**vaso
poroso**

**cilindro
di rame**

$\text{CuSO}_4(\text{s})$

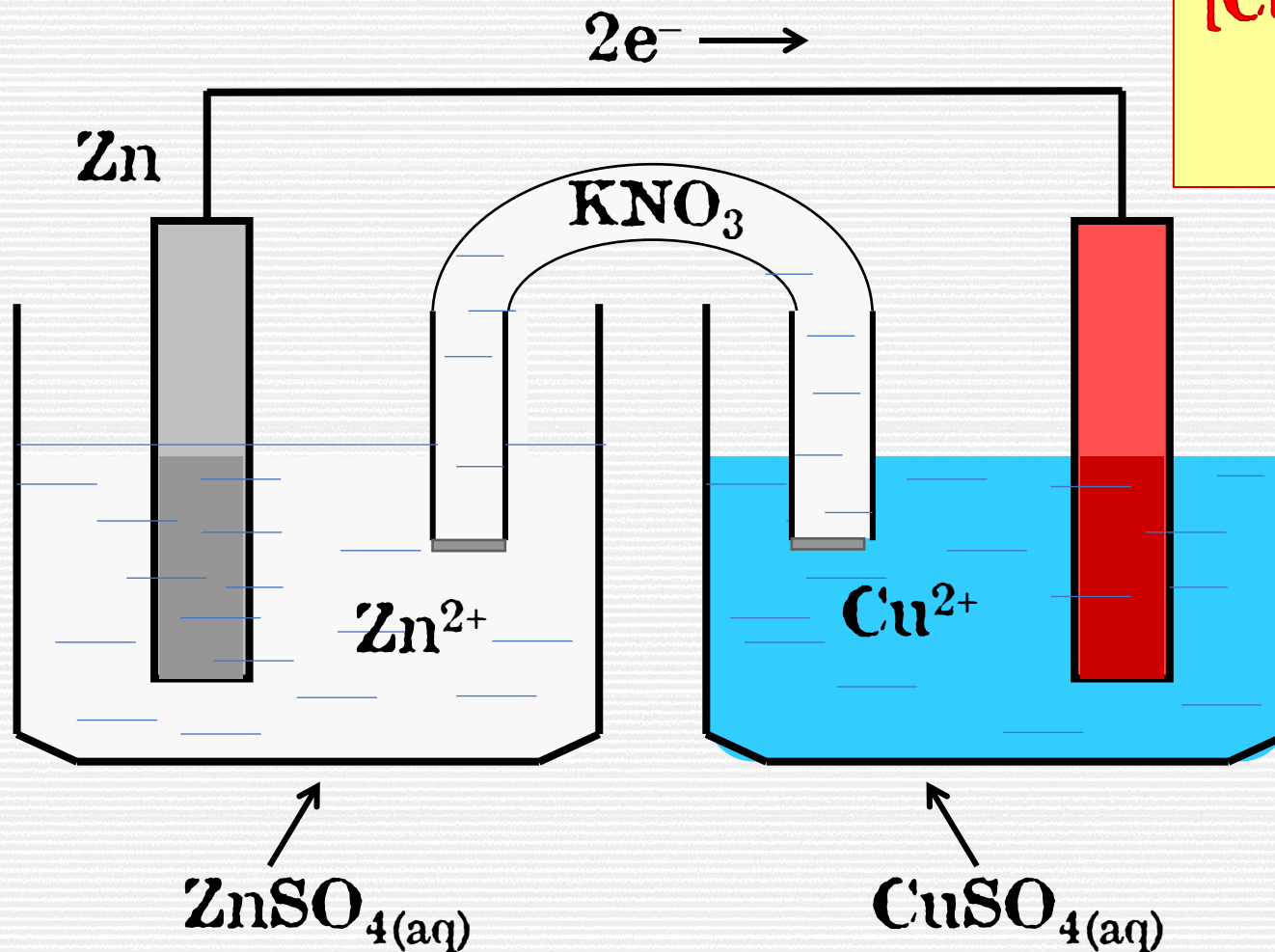
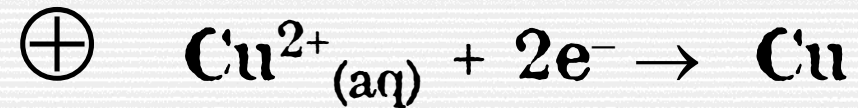




Batterie di celle Daniell vennero usate fino al 1860 per alimentare le reti telegrafiche

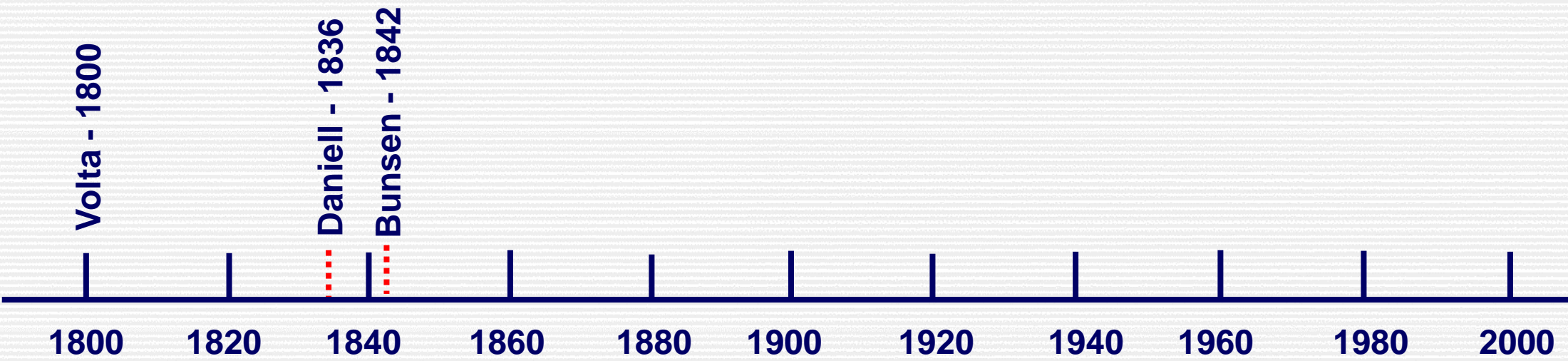
Daniell cell batteries, 1836, by John Frederic Daniell (England). Exhibit in National Museum of American History, Washington, DC, USA.

Cella Daniell – versione didattica



$[\text{Cu}^{2+}] = [\text{Zn}^{2+}] = 1 \text{ M}$
 $T = 25 \text{ }^{\circ}\text{C}$
 $\Delta E^{\circ} = 1.10 \text{ V}$

Cronologia delle 'pile'





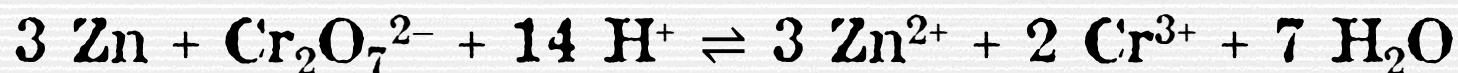
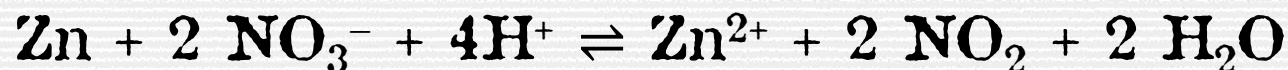
Robert Wilhelm Bunsen (1811-1899)

Professore a Heidelberg (1852-1889)

- ❑ Spettroscopia di emissione degli elementi (con Kirchhoff)
- ❑ Scoperta e isolamento di cesio e rubidio

Dottorandi: Adolf von Baeyer, Hans Goldschmidt, Fritz Haber, Lothar Meyer, Dmitri Mendeleev, Friedrich Konrad Beilstein, Henry Roscoe, John Tyndall, Edward Frankland.

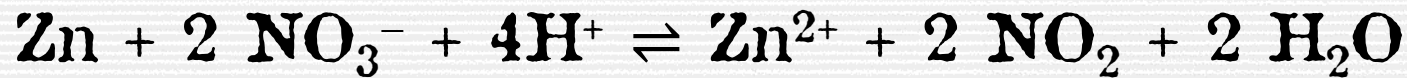
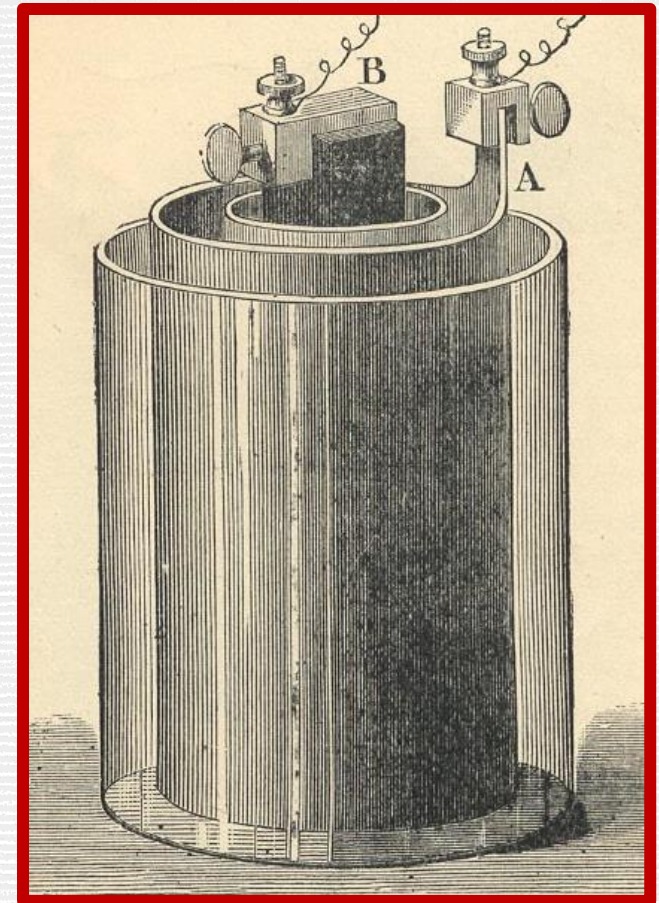
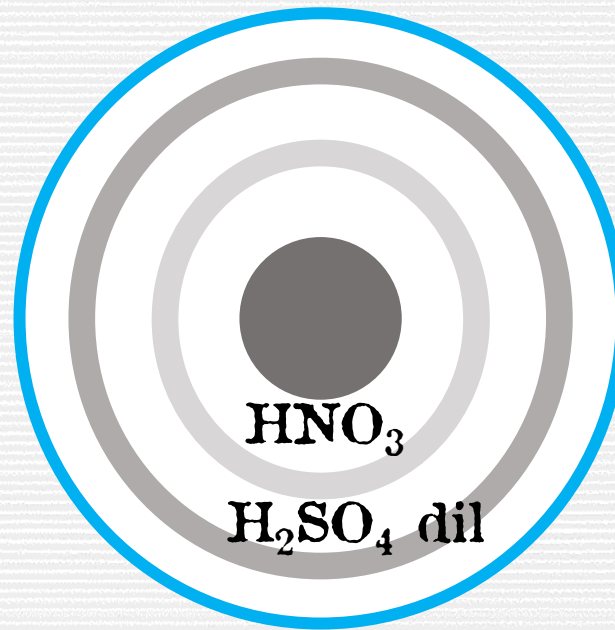
R. Bunsen, "Über die Anwendung der Kohle zu Volta'schen Batterien (Sull'uso del carbone nelle batterie voltaiche)" *Annalen der Physik und Chemie* 1841, 130, 417–430



elettrodo donatore: zinco

Cella di Bunsen

- ☐ vetro
- ☐ zinco
- ☐ ceramica porosa
- ☐ grafite



$$E^\circ = -0.76 \text{ V}$$

$$E^\circ = \sim 0.8 \text{ V}$$

$$\Delta E^\circ = \sim 1.6 \text{ V}$$

Henri Moissan (1852-1907) used a stack of 90 cells for the electrolysis of hydrogen fluoride to obtain fluorine for the first time (1886).

Periodic Table Of The Elements

1	1 H Hydrogen 1.008	2	13	5 B Boron 10.811	14	6 C Carbon 12.011	15	7 N Nitrogen 14.007	16	8 O Oxygen 15.999	17	9 F Fluorine 18.998	18	2 He Helium 4.003
2	3 Li Lithium 6.941	4 Be Beryllium 9.012	10	11 Na Sodium 22.990	12	12 Mg Magnesium 24.305	19	20 K Potassium 39.098	36	35 Br Bromine 79.904	54	53 I Iodine 126.905	86	85 At Astatine [210]
3	11 Na Sodium 22.990	12 Mg Magnesium 24.305	19	20 K Potassium 39.098	37	38 Sr Strontium 87.62	55	56 Cs Cesium 132.905	87	88 Ra Radium 226.025	118	117 Ts Tennessine [294]	150	149 Uue Ununennium [289]
4	19 K Potassium 39.098	20 Ca Calcium 40.078	37	38 Sr Strontium 87.62	55	56 Cs Cesium 132.905	87	88 Ra Radium 226.025	118	117 Ts Tennessine [294]	150	149 Uue Ununennium [289]	188	187 Uuh Ununhennium [289]
5	37 Rb Rubidium 85.468	38 Sr Strontium 87.62	55	56 Cs Cesium 132.905	87	88 Ra Radium 226.025	118	117 Ts Tennessine [294]	150	149 Uue Ununennium [289]	188	187 Uuh Ununhennium [289]	226	225 Uuq Ununquadium [289]
6	55 Cs Cesium 132.905	56 Ba Barium 137.328	87	88 Ra Radium 226.025	118	117 Ts Tennessine [294]	150	149 Uue Ununennium [289]	188	187 Uuh Ununhennium [289]	226	225 Uuq Ununquadium [289]	264	263 Uus Ununseptium [289]
7	87 Fr Francium 223.020	88 Ra Radium 226.025	118	117 Ts Tennessine [294]	150	149 Uue Ununennium [289]	188	187 Uuh Ununhennium [289]	226	225 Uuq Ununquadium [289]	264	263 Uus Ununseptium [289]	302	301 Uuo Ununoctium [289]

Number
Symbol
Name
Atomic Mass

LA VOLETE SMETTERE DI POMPARE
ELETTRONI DALLLO ZINCO? NON
AVETE VISTO LA TAVOLA
APOCALITTICA DEGLI ELEMENTI?

62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
95 Am Americium [243]	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]	

©2018 sciencenotes.org

Alkaline metal

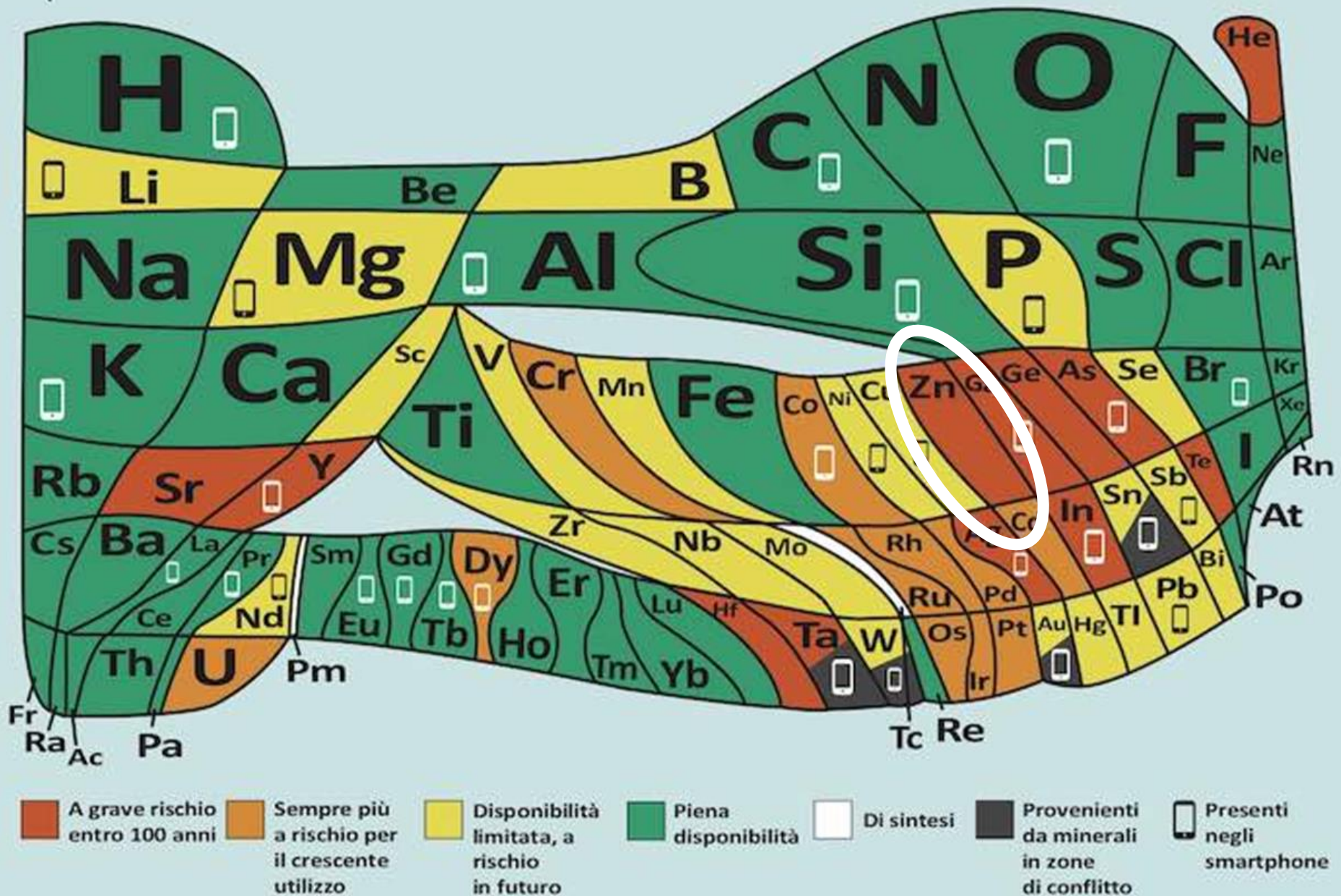
Halogen

Noble Gas

Lanthanoid

Actinoid

TAVOLA APOCALITTICA DEGLI ELEMENTI

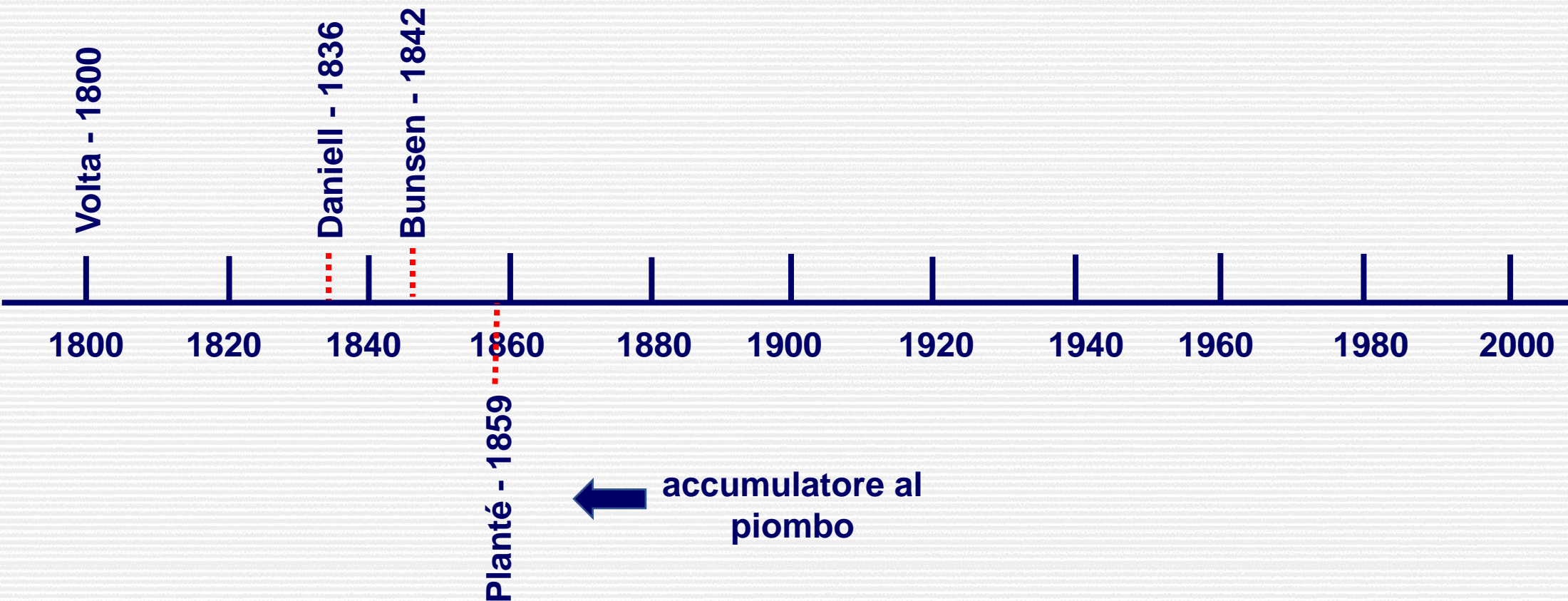


Scopri di più e divertiti con il videogioco su <http://bit.ly/euchems-pt>



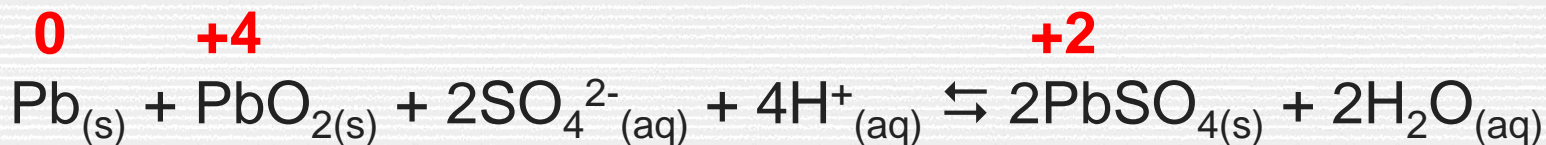
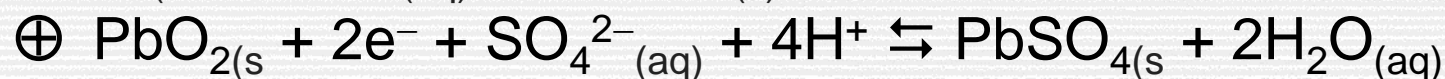
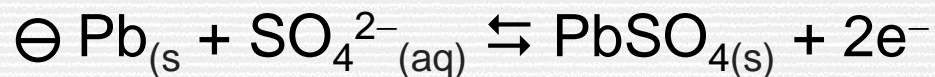
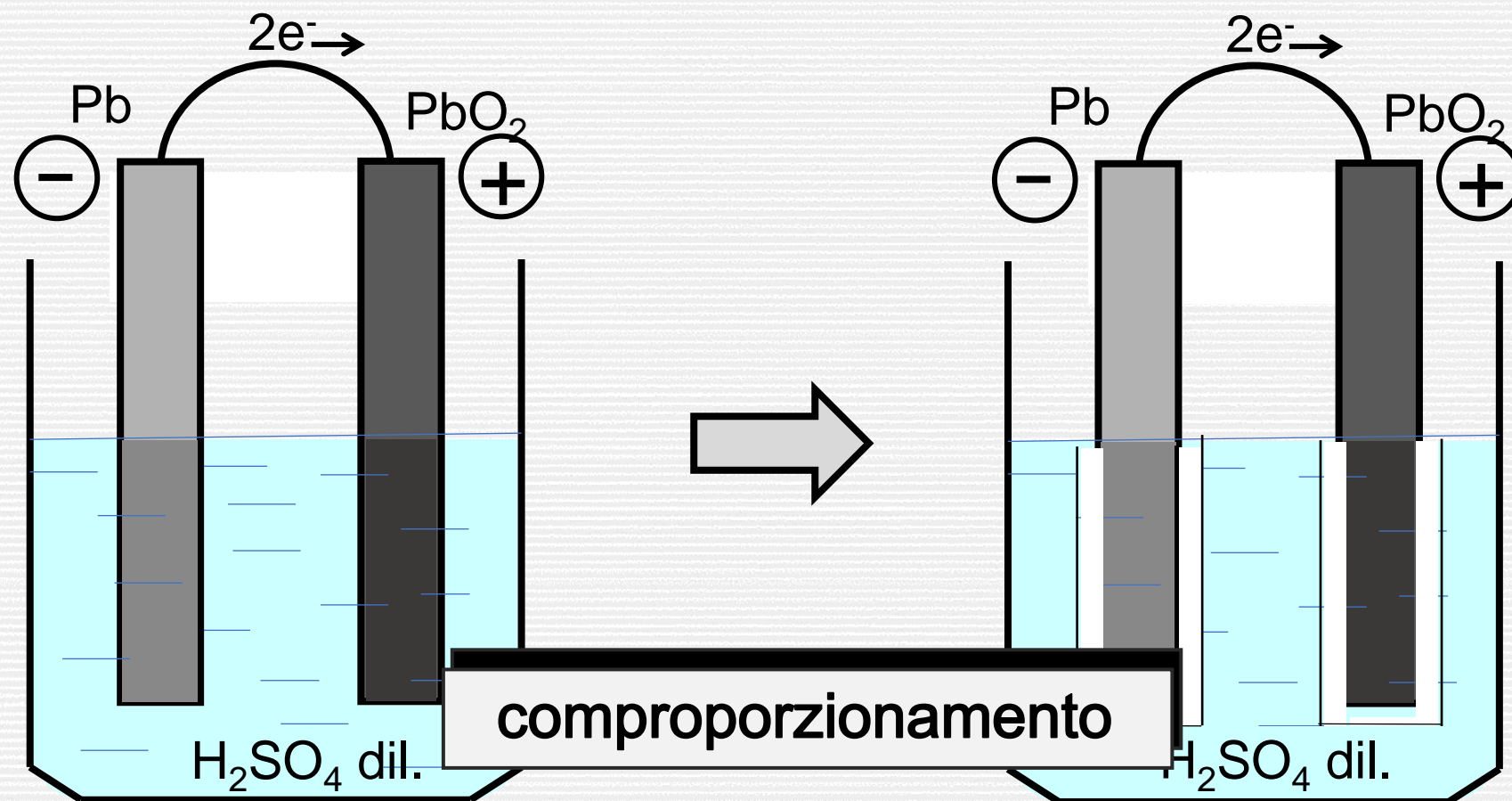
Quest'opera è rilasciata con licenza Creative Commons Attribution-NoDerivs CC-BY-ND

batterie non ricaricabili



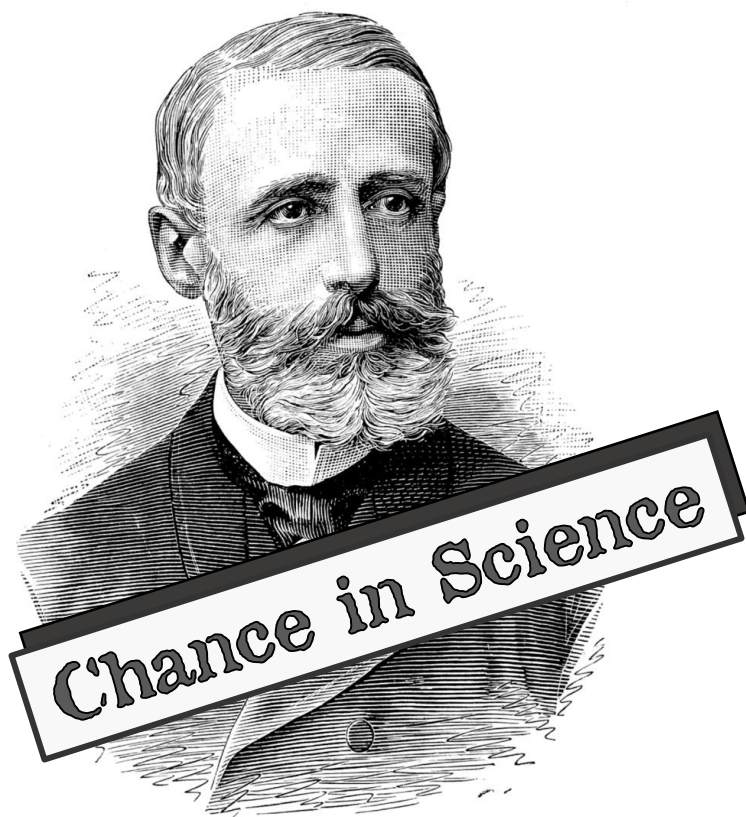
batterie ricaricabili

Cella Planté (accumulatore al piombo)– versione 'didattica'



scarica →

← ricarica



Gaston Planté (1834-1889)
Professeur de Physique à
l'Association Polytechnique
pour le Développement de
l'Instruction Populaire, Paris

RECHERCHES
SUR
L'ÉLECTRICITÉ

PAR
GASTON PLANTÉ

Licencié ès sciences physiques,
Ancien Professeur de Physique à l'Association polytechnique.
Lauréat de l'Institut (Académie des sciences),
Membre correspondant de l'Académie royale des sciences de la Havane,
Membre de l'*American philosophical Society* de Philadelphie, etc.

de 1859 à 1879

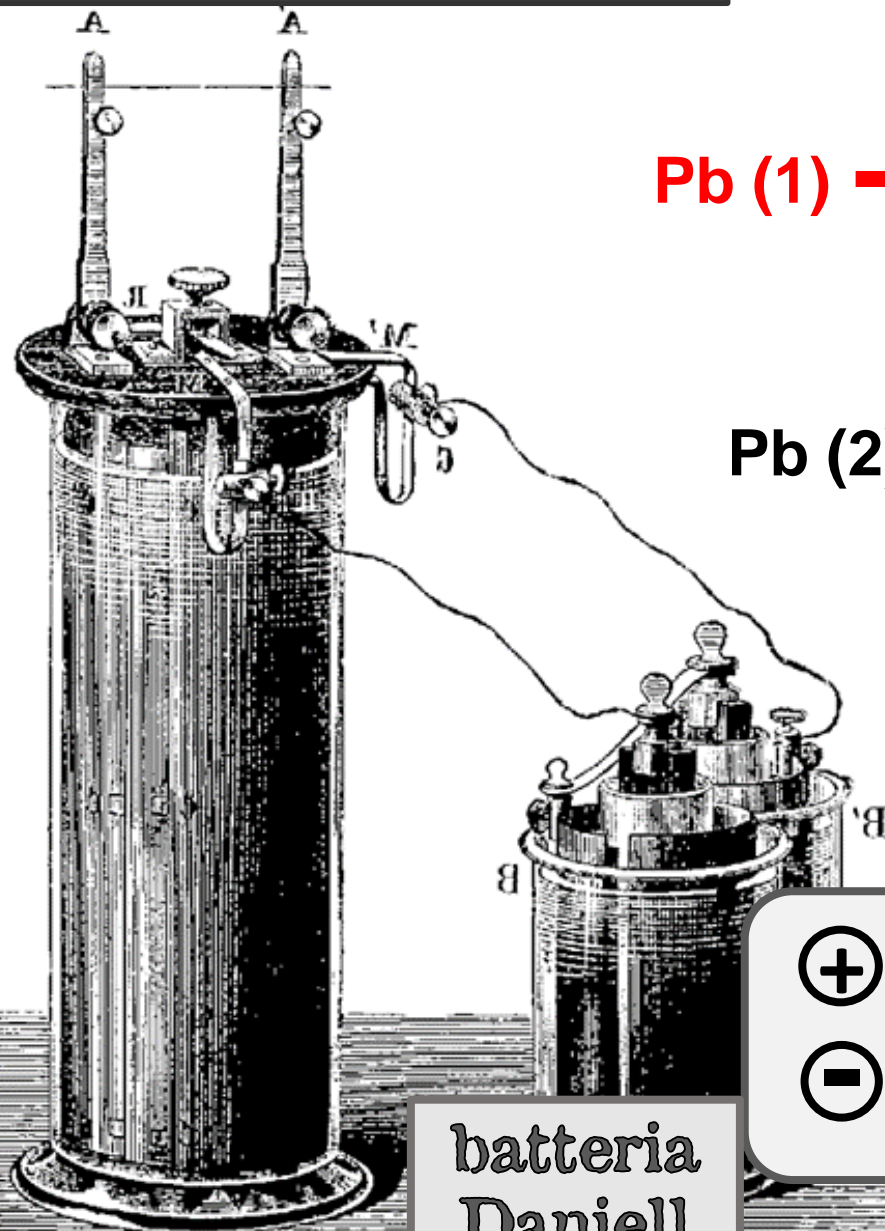
(AVEC 89 FIGURES DANS LE TEXTE)

OUVRAGE RÉIMPRIMÉ
SUR LE TEXTE DE LA PREMIÈRE ÉDITION PUBLIÉE
EN FÉVRIER 1879 ET COMPRENANT LES DEUX FASCICULES
SUPPLÉMENTAIRES PUBLIÉS PAR L'AUTEUR
EN OCTOBRE 1879.

PARIS
AUX BUREAUX DE LA REVUE LA LUMIÈRE ÉLECTRIQUE
54, RUE VIVIENNE, 54

1883

Elettrolisi su due
elettrodi di Pb in
 H_2SO_4 dil



batteria
Daniell

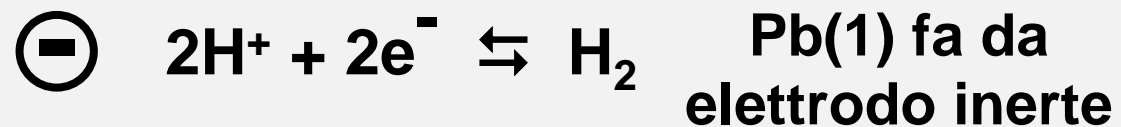
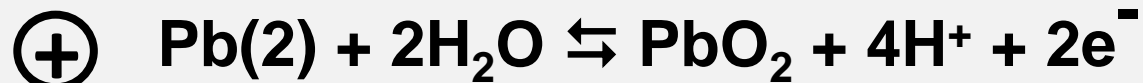
vetro

Pb (1)

Pb (2)

H_2SO_4 dil.

elettrodi: 2 bande di piombo
a spirale, **Pb(1)** e Pb(2),
inserite l'una nell'altra



ho ottenuto,
senza volere, una
cella galvanica

Pb

PbO₂

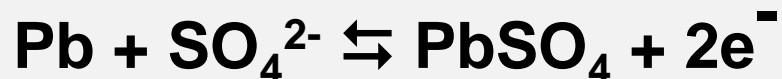
H₂SO₄ dil.

$$\Delta E = \sim 2 \text{ V}$$

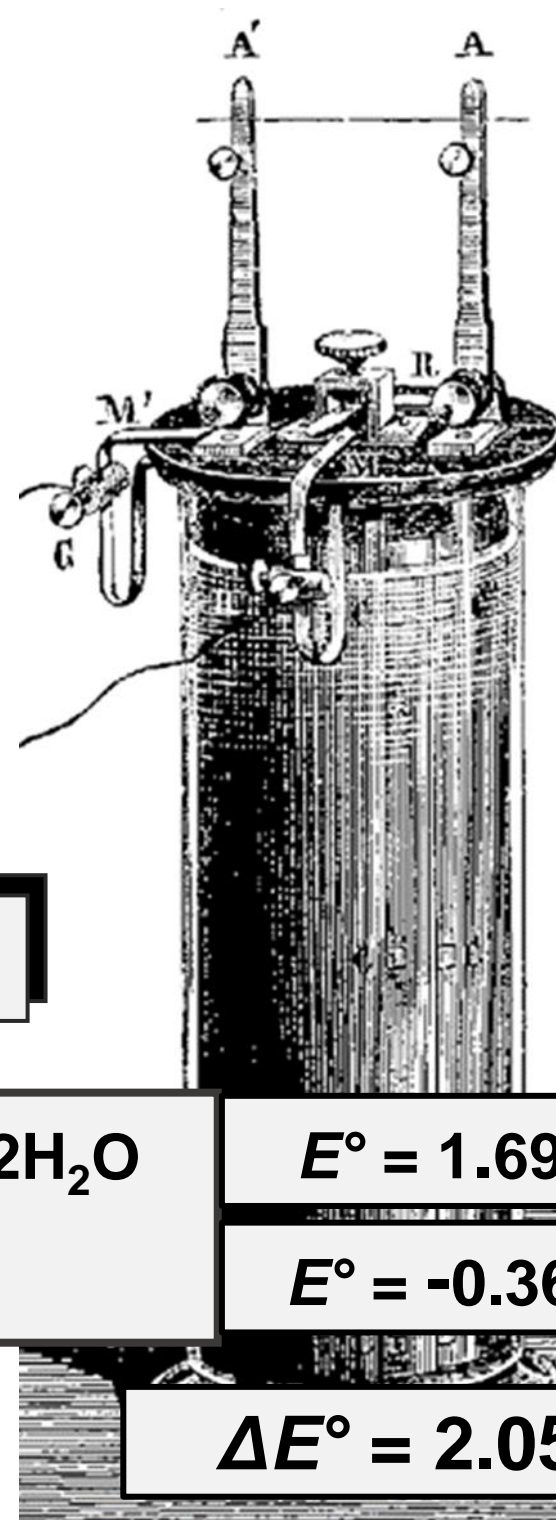
⊕



⊖



La cella, una volta esaurita, può
essere ricaricata



$$E^\circ = 1.69 \text{ V}$$

$$E^\circ = -0.36 \text{ V}$$

$$\Delta E^\circ = 2.05 \text{ V}$$

CHAPITRE II

Accumulation de la force de la pile voltaïque, à l'aide de couples secondaires à lames de plomb.

37. — Couple secondaire à lames de plomb en spirale. — C'est ainsi que nous fûmes conduit à construire, en 1860 ⁽¹⁾, un élément secondaire de grande intensité, en employant une lame à celle qu'Offer-

ient employée pour proprement dite, enroulant en spirale



Fig. 7.

La batteria Planté serve a poco:
può solo accumulare l'energia
prodotta da un'altra batteria

deux longues et larges lames de plomb, séparées l'une de l'autre par une toile grossière, et les plongeant ensuite dans un bocal plein d'eau acidulée au $\frac{1}{10}$ par l'acide sulfurique.

(1) *Comptes rendus*, t. L., p. 640. Mars 1860.

SCOPO LUDICO

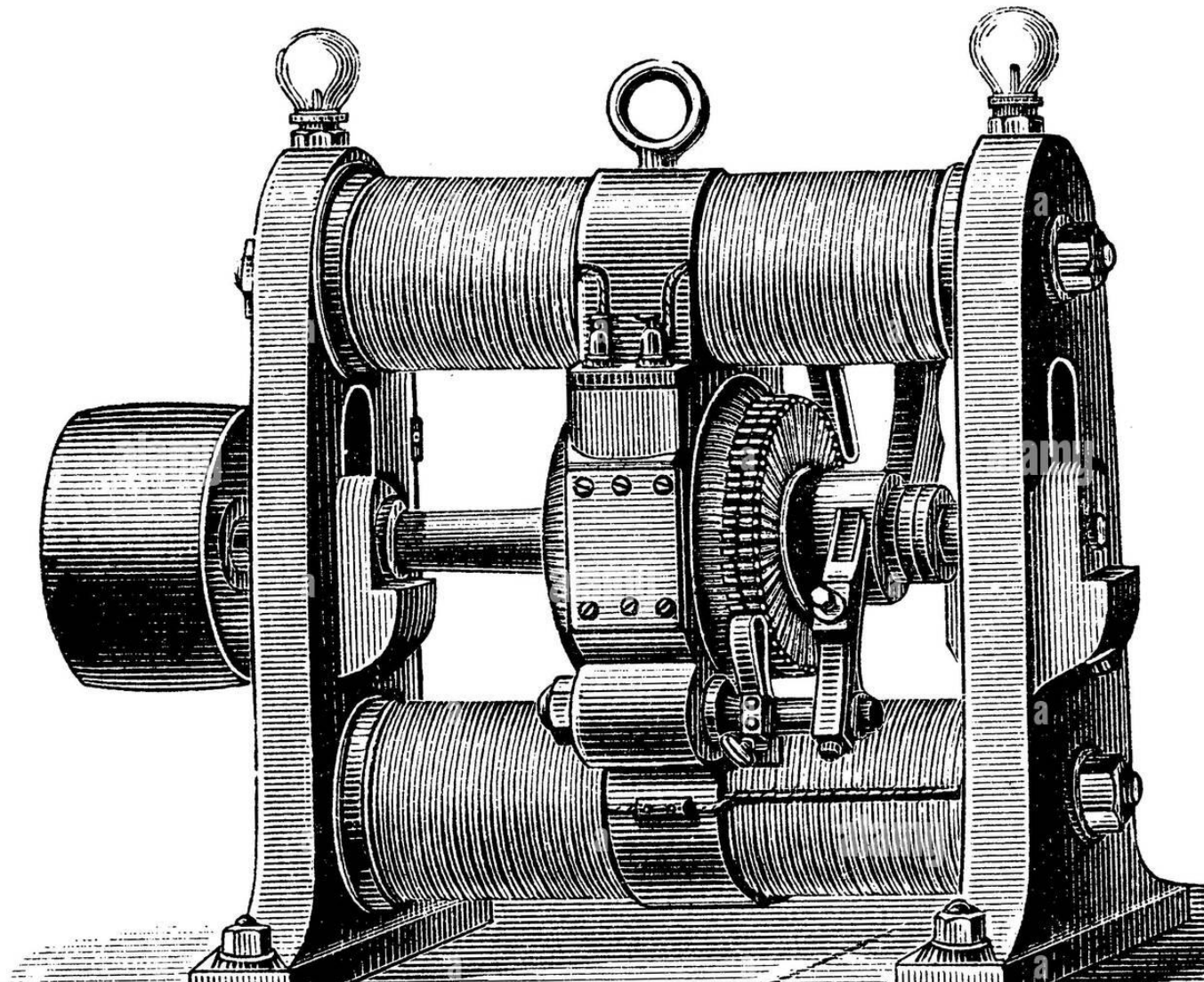
scarica elettrica

batteria
Planté

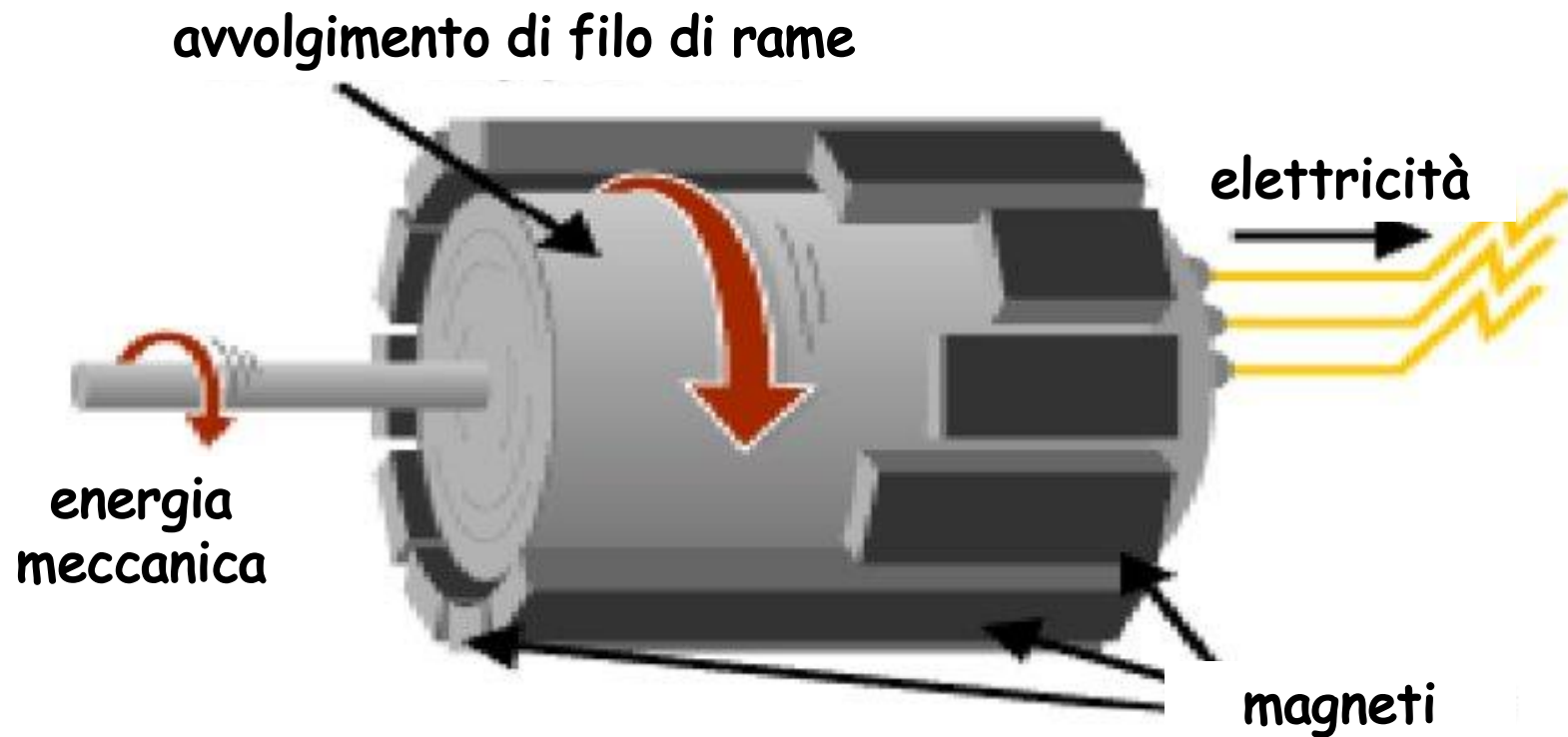
batteria
Daniell

Louis Figuier, Les Merveilles de la science ou description populaire des inventions modernes, Librairie Furne, Editeurs Jouvot et Cie, 1867-1891.

fino a che... non viene inventata una macchina capace di convertire energia meccanica in energia elettrica: la dinamo



Dinamo (Pacinotti, Gramme, Edison) 1860-1880



Le batterie reversibili, tipo Planté, possono essere caricate con energia meccanica. Diventano dei 'serbatoi' di energia elettrica. Non si consumano materiali



**con gli accumulatori
nascono le auto
elettriche**

Camille Jenatton (1868-1913), ingénieur et coureur automobile belge, connu surtout pour avoir été le premier à dépasser les 100 km/h, le 29 avril 1899, à bord d'une voiture de sa conception, «La Jamais Contente», une **voiture électrique en forme d'obus ou de torpille. Son nom de famille dérive de **l'italien Genazzi**, son aïeul ayant migré à Bastogne au XVIII^e siècle.**

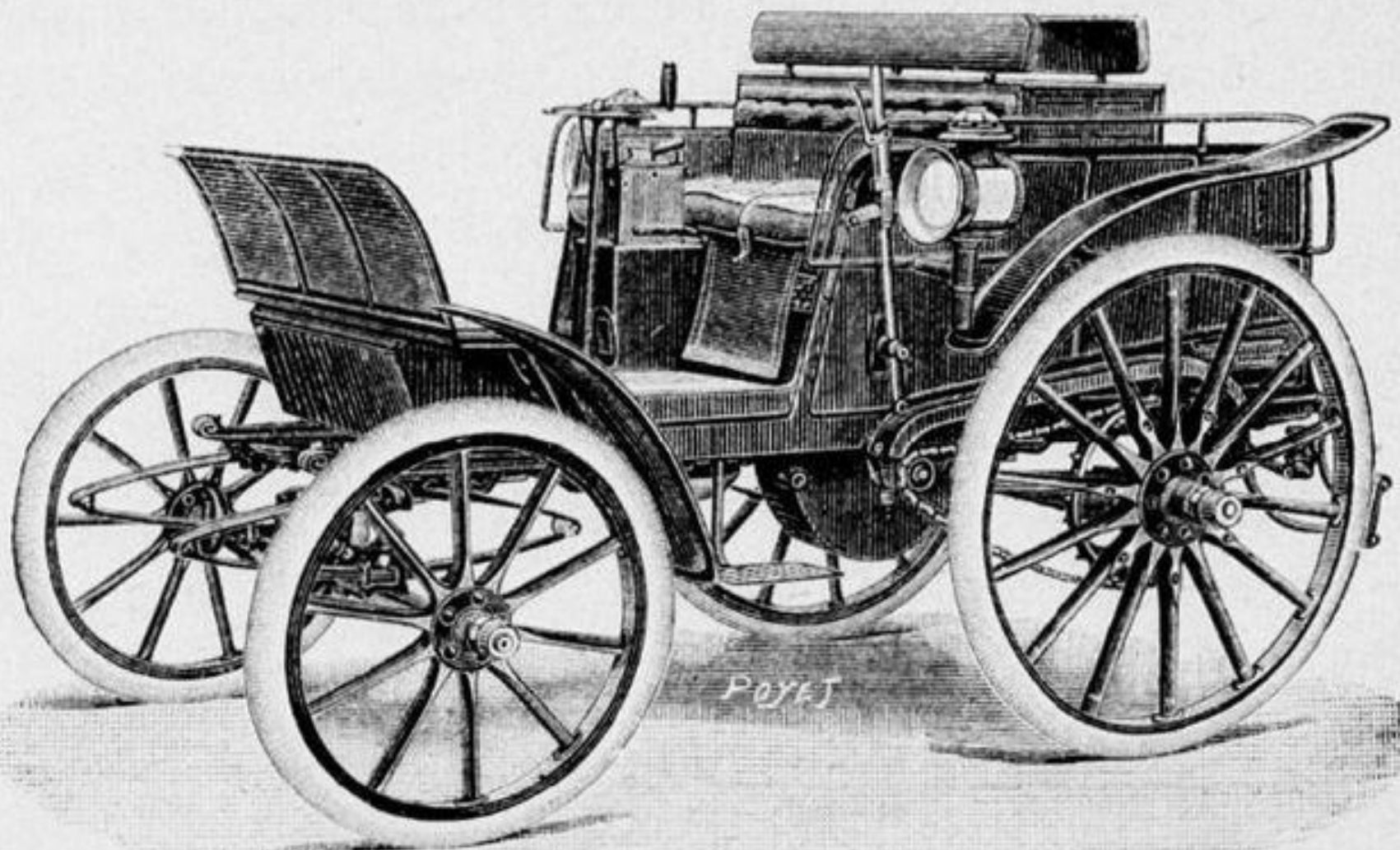


Camille Jenatzy (*Le Diable Rouge*) et sa femme en 1899 aux Tuileries lors de la célébration du record établi avec *La Jamais Contente* (106 km/h). La voiture était alimentée par une batterie au plomb, faite des 100 accumulateurs ($100 \times 2 \text{ V} = 200 \text{ V}$)

AUTOMOBILES ÉLECTRIQUES JENATZY

Les plus perfectionnées

DÉTENTEUR des RECORDS du MONDE
de 1 kilomètre en côte (Chanteloup), en 3" 52"
de 2 kilomèt. vitesse (Achères), en 1' 41" $\frac{2}{5}$



USINE A BOULOGNE-SUR-SEINE

Envoi franco de Devis et Renseignements

Compagnie Internationale des Transports Automobiles } Société anonyme au capital de 1.000.000
56, rue de la Victoire, PARIS

SI', MA IO VOGLIO
UNA BATTERIA PICCOLINA,
LEGGERA, USA-E-GETTA,
PER ALIMENTARE IL MIO
I-PHONE. E SOPRATTUTTO
CHE NON PERDA LIQUIDI.
INSOMMA, VOGLIO
UNA PILA A SECCO



G. Zamboni, «Della pila elettrica **a secco**», *Giornale di Fisica, Chimica e Storia Naturale* 1812, 5, 424.

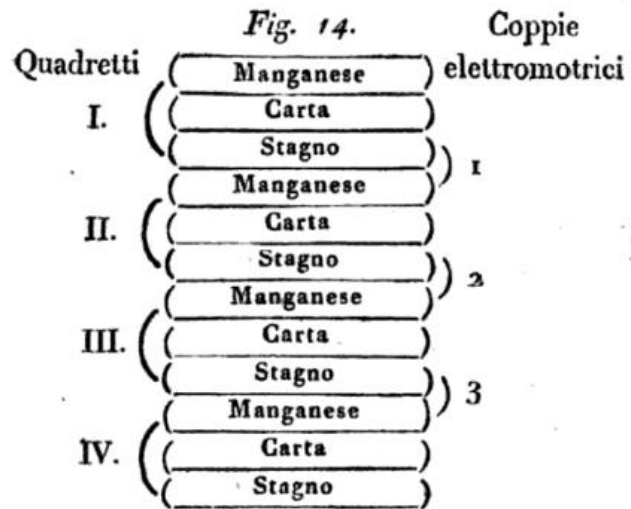


Giuseppe Zamboni

Arbizzano 1776 – Verona 1846

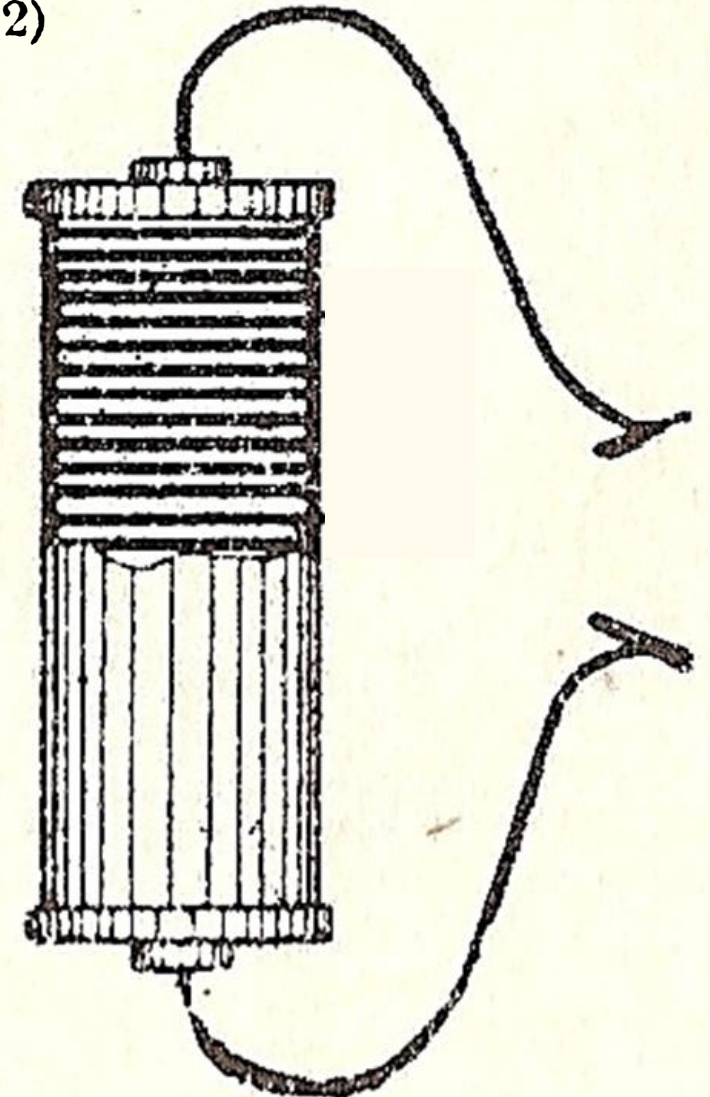
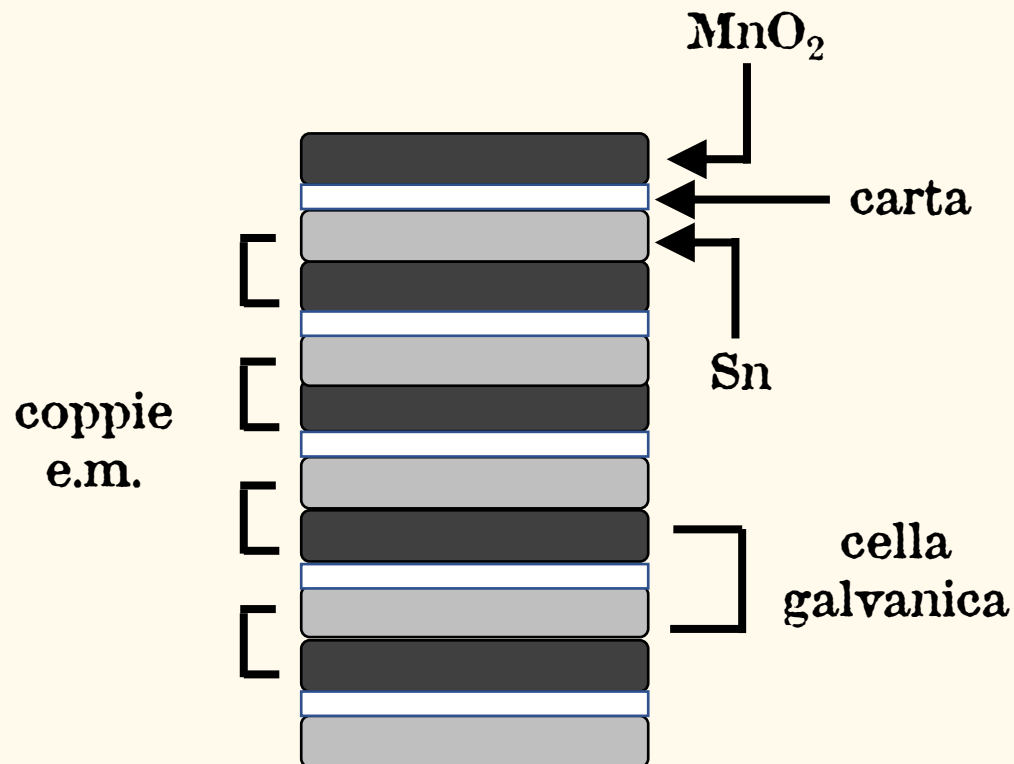
abate, fisico

docente presso l'*Imperial Regio Liceo* di Verona

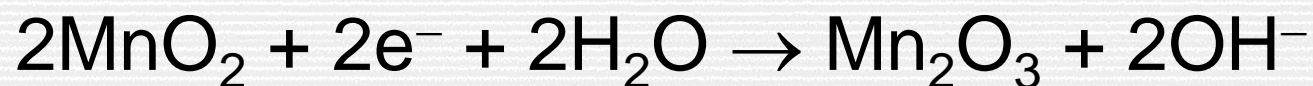
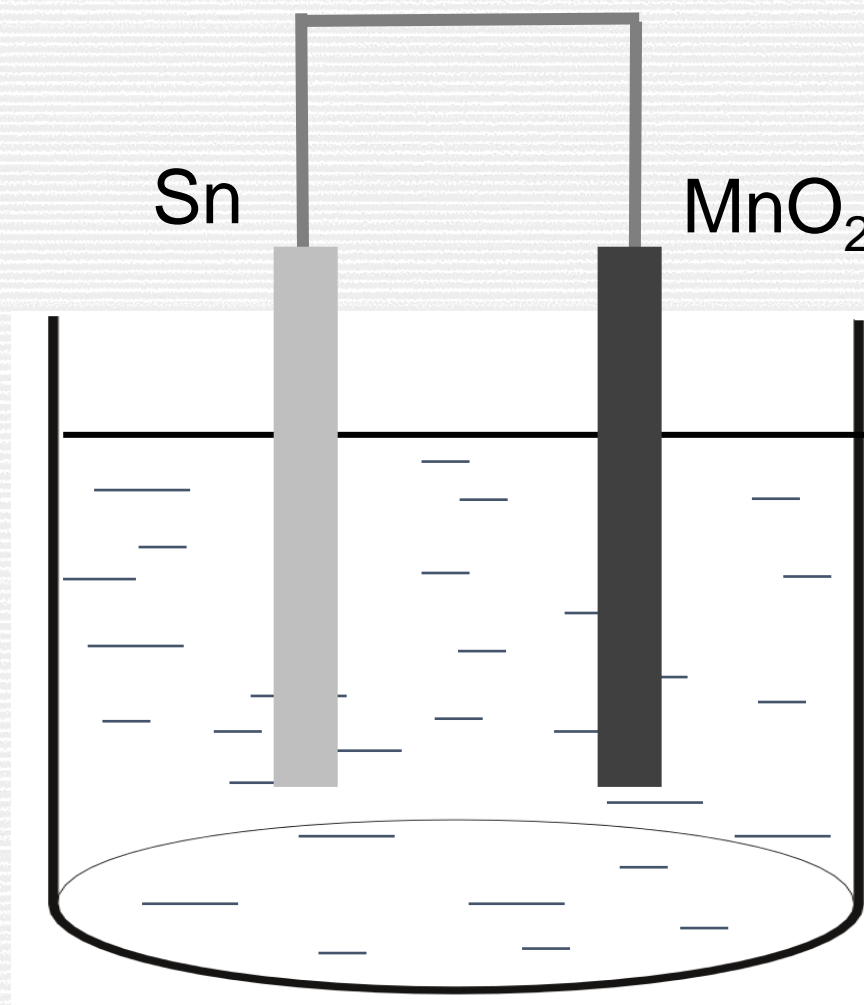


dischetti di carta che interfacciano un dischetto di foglio di Sn (o Zn) e uno strato di MnO_2 impastato con colla (suggerito da A. Volta).

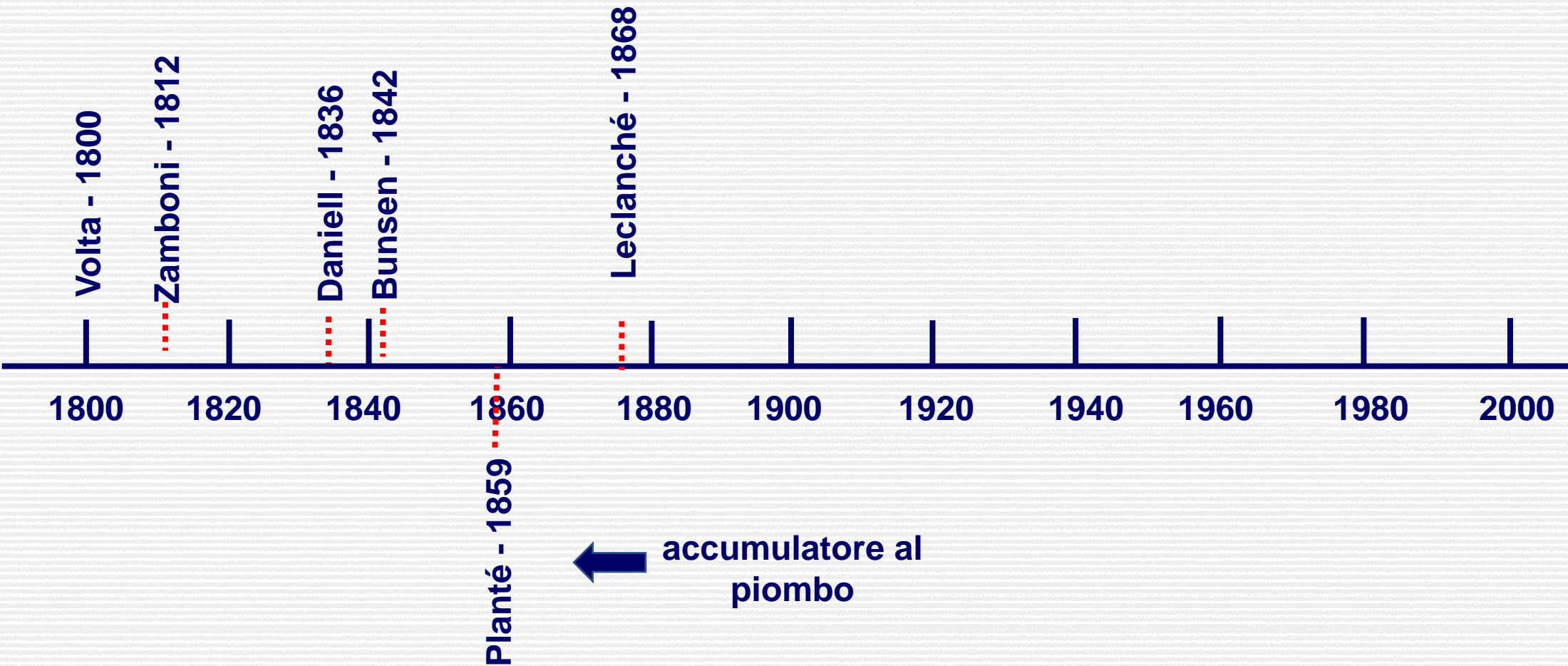
«... manganese nero di ottima qualità supera di assai nella facoltà elettromotrice e la piombaggine [*Mo, ndr*] e il miglior carbone». Lettera di A. Volta a G. Zamboni (1812)



La cella di Zamboni (versione didattica)



batterie non ricaricabili



batterie ricaricabili



Georges Leclanché

1839–1882

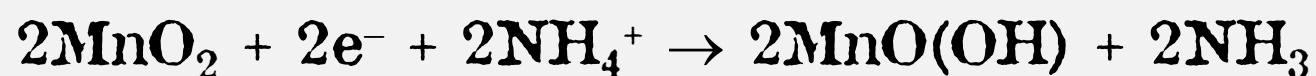
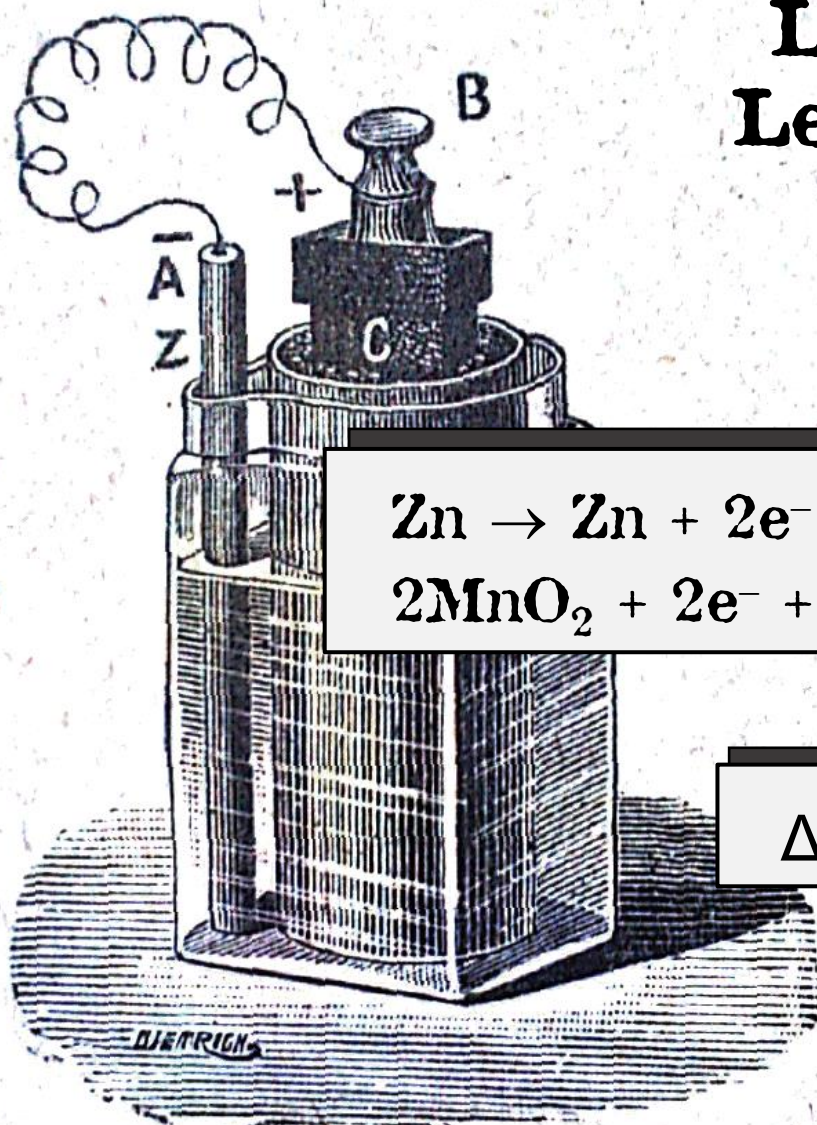
Ingegnere e industriale francese

G. Leclanché, "*une pile à oxyde insoluble*"
Brevet français no. 71 865 (publié le 8 juin
1866)

Leclanché, Georges (1867). *Notes sur
l'emploi des piles électriques en
télégraphie, pile constante au peroxyde de
manganèse à un seul liquide*. Paris: Impr.
de Hennuyer et fils.

Leclanché, Georges (1869). *Notice sur la
pile Leclanché : précédée de quelques
considérations sur l'emploi des piles
électriques en télégraphie*. Paris: Jamin,
Bailly et cie, Librairie Burndy

La cella Leclanché



$$\Delta E = 1.5 \text{ V}$$

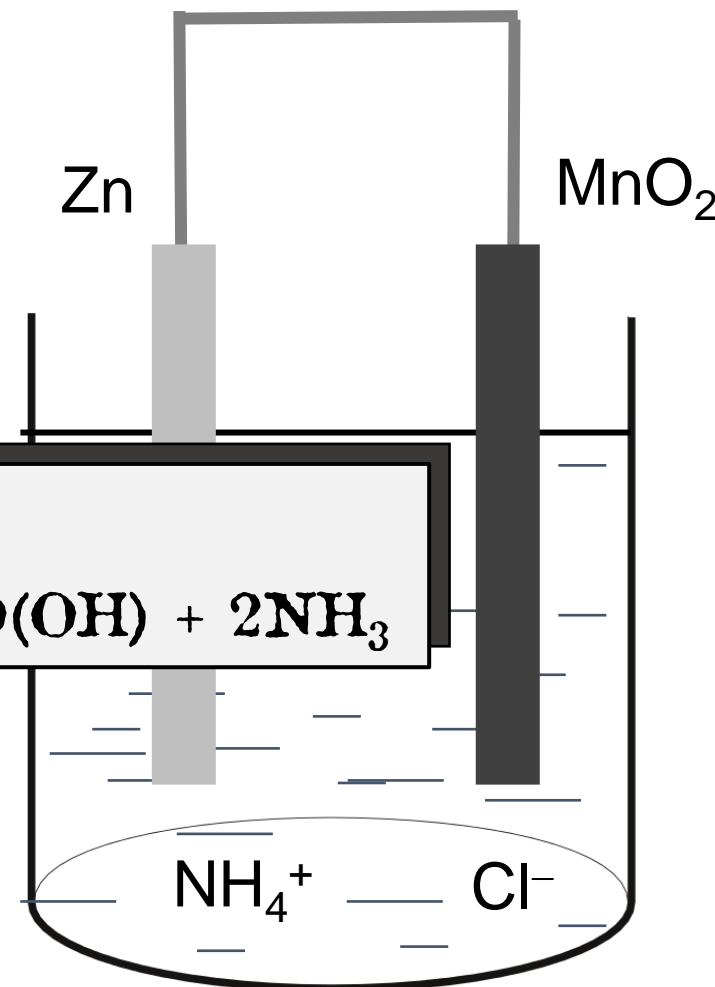


FIG. 153. — Pile Leclanché. —
V, vase de verre renfermant une solu-
tion saturée de sel ammoniac; Z, cy-
lindre de zinc amalgamé; T, vase po-
reux renfermant du bioxyde de manga-
nèse (MnO_2); C, charbon de cornue.

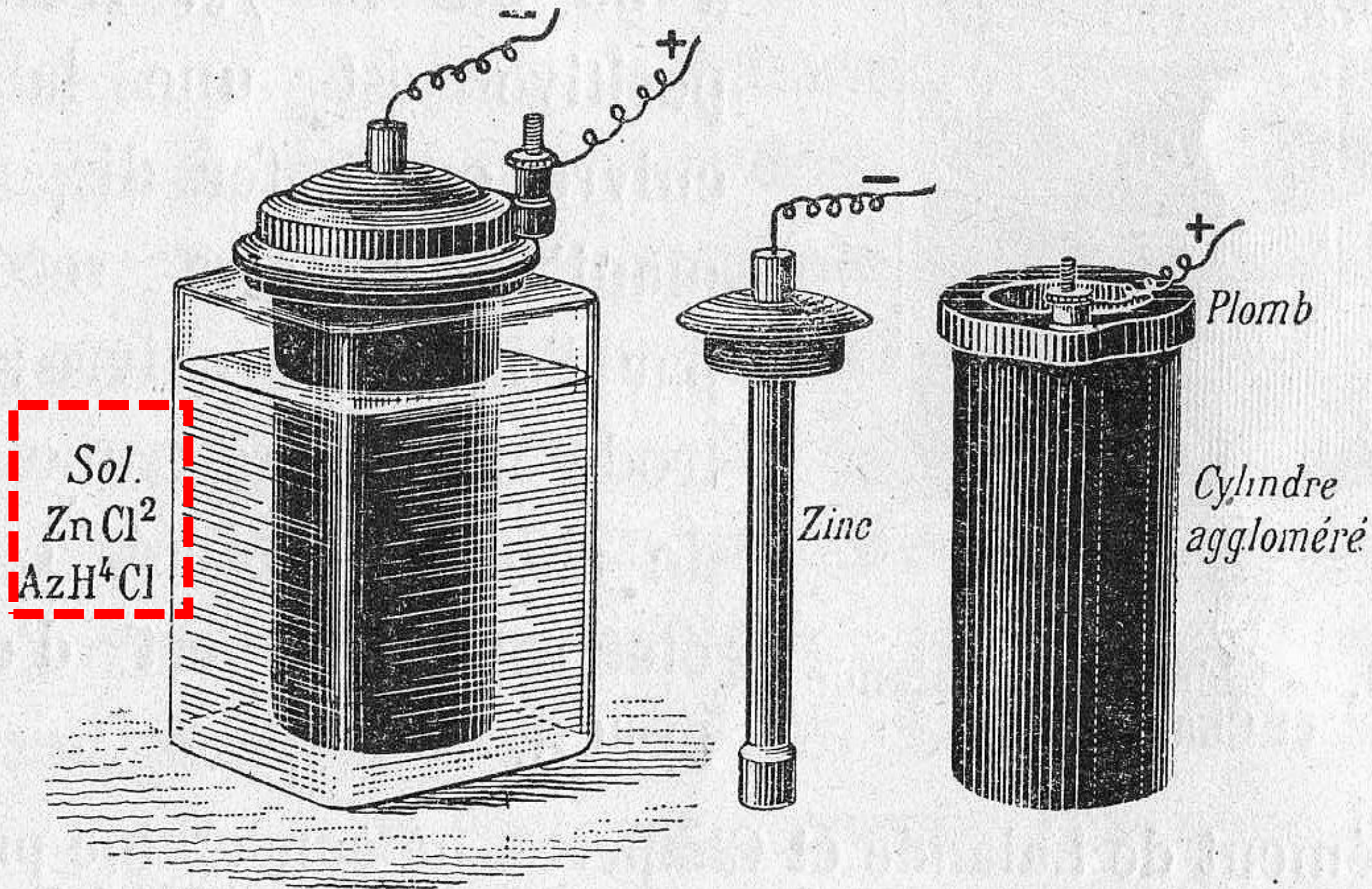
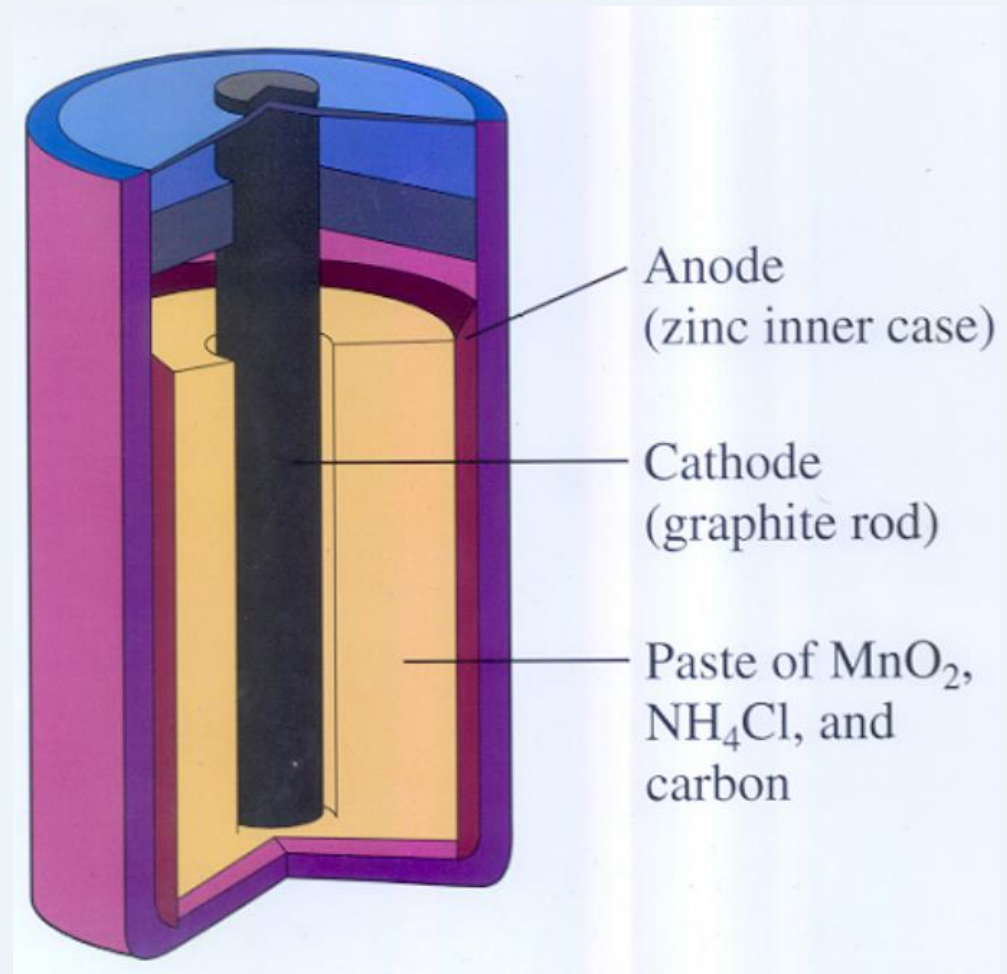


Fig. 293. — Élément Leclanché-Barbier.

pile saline → pile sèche (industrie Leclanché)

- ❑ La soluzione di NH_4Cl viene gelificata con amido.
- ❑ La pila diviene trasportabile.
- ❑ Viene prodotta industrialmente e messa in commercio.

versione finale



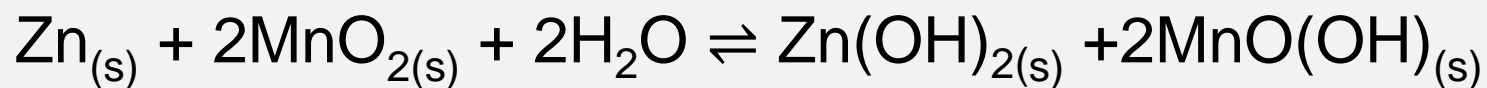
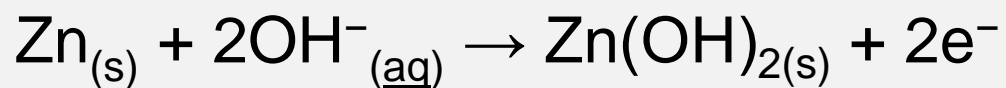
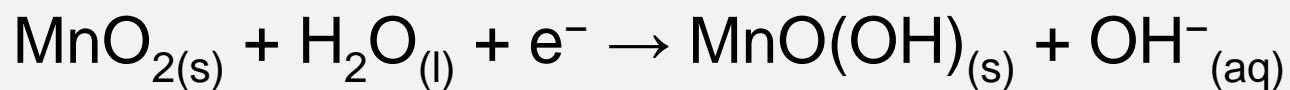
1960



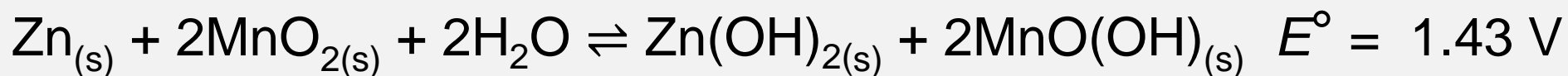
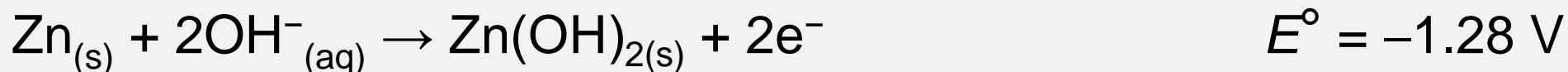
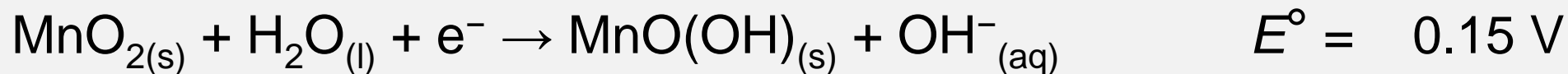
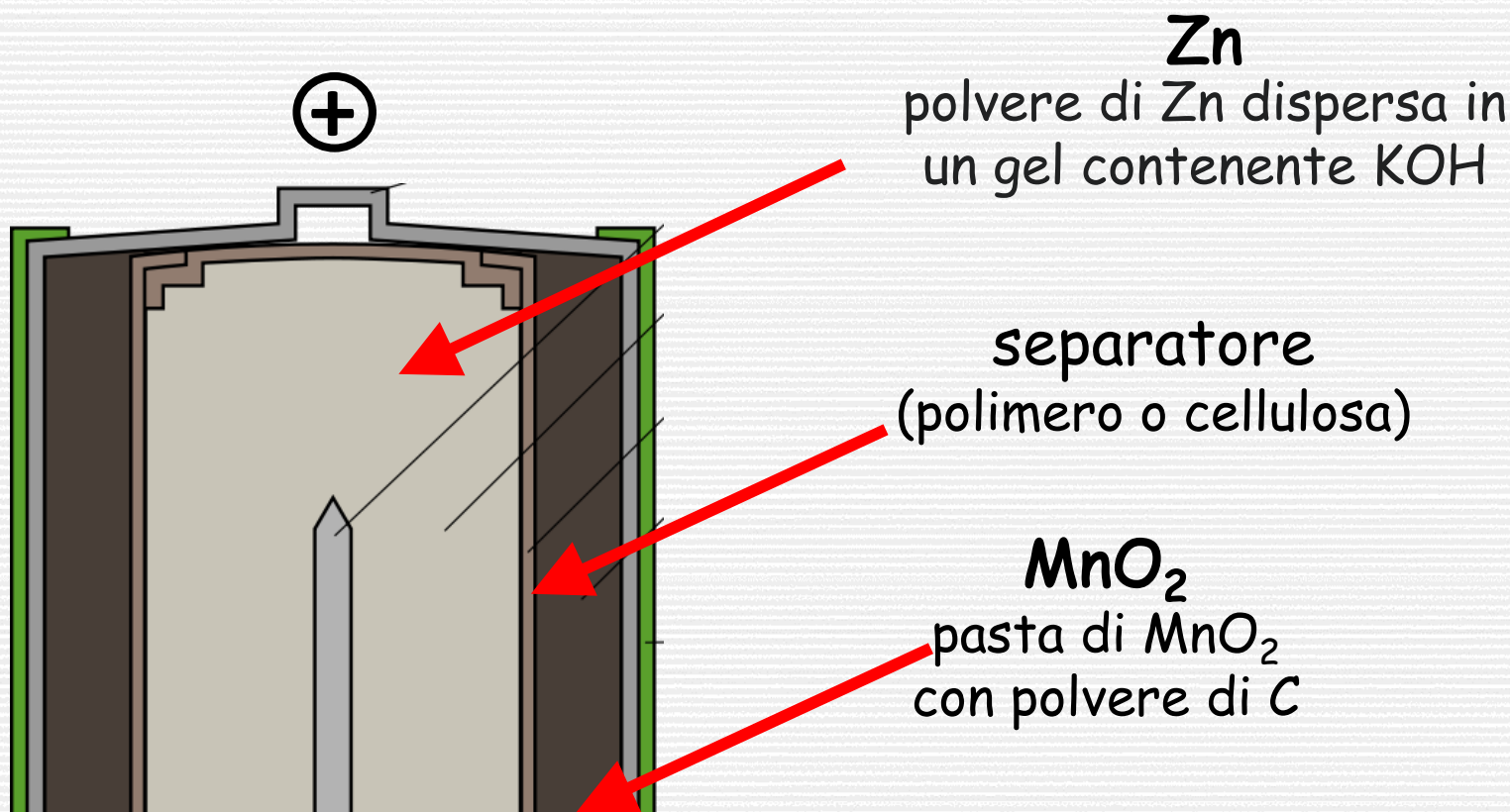
zinco-carbone



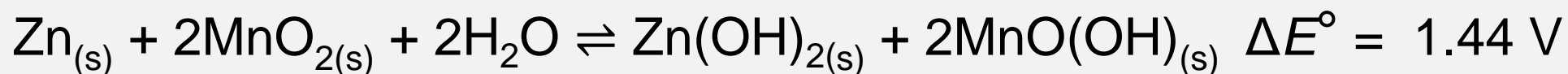
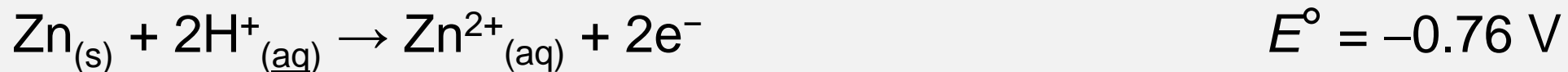
alcalina



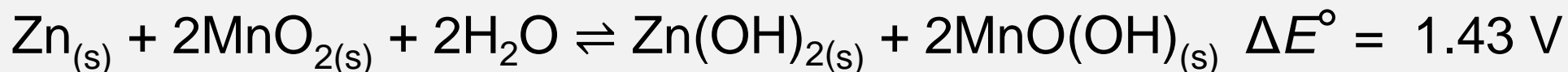
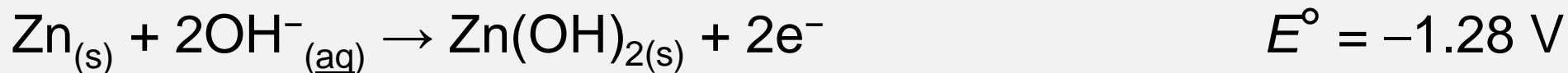
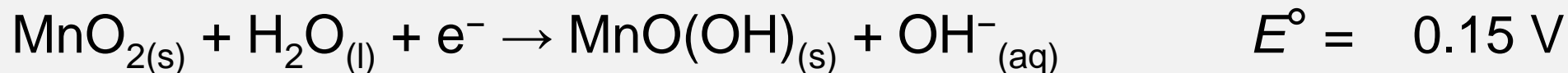
La batteria alcalina (brevetto Union Carbide 1960)



zinco-carbone



alcalina



E DOVE STA IL VANTAGGIO ?



- ☐ Le Batterie Alcaline (BA) hanno una più alta densità energetica, a parità di prestazione pesano di meno.
- ☐ A differenza delle batterie Zinco-Carbone (ZC), le BA resistono meglio alle basse temperature.
- ☐ Le BA non sono soggette alla perdita di liquido come le ZC e garantiscono un trasporto più sicuro.
- ☐ Le BA presentano una minor resistenza interna delle ZC e forniscono una corrente Maggiore.

Ma la reazione $2\text{H}_2 + \text{O}_2$
è una ossido-riduzione?

Se riesci a farne
una batteria, sì



Jacques-Louis David (1788)
*Portrait d'Antoine-Laurent
Lavoisier et de sa femme*
peinture à l'huile, 260 × 195 cm
Metropolitan Museum of Art,
New York

William Robert Grove (1811-1896)

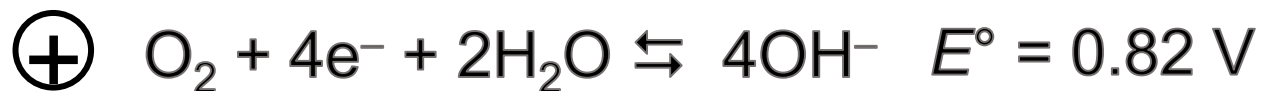
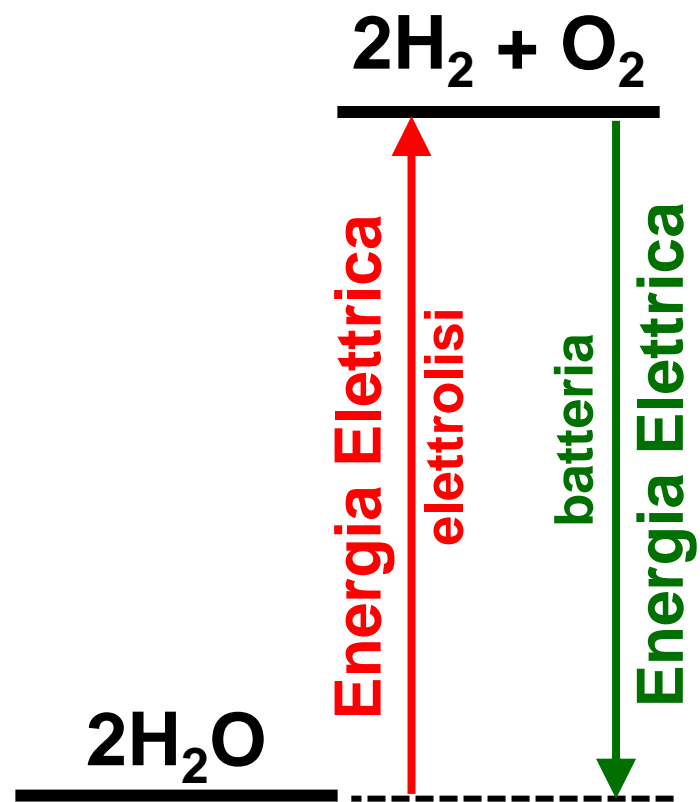
Welsh judge and physical scientist. He anticipated the general theory of the conservation of energy and was a pioneer of fuel cell technology. He invented the Grove voltaic cell.



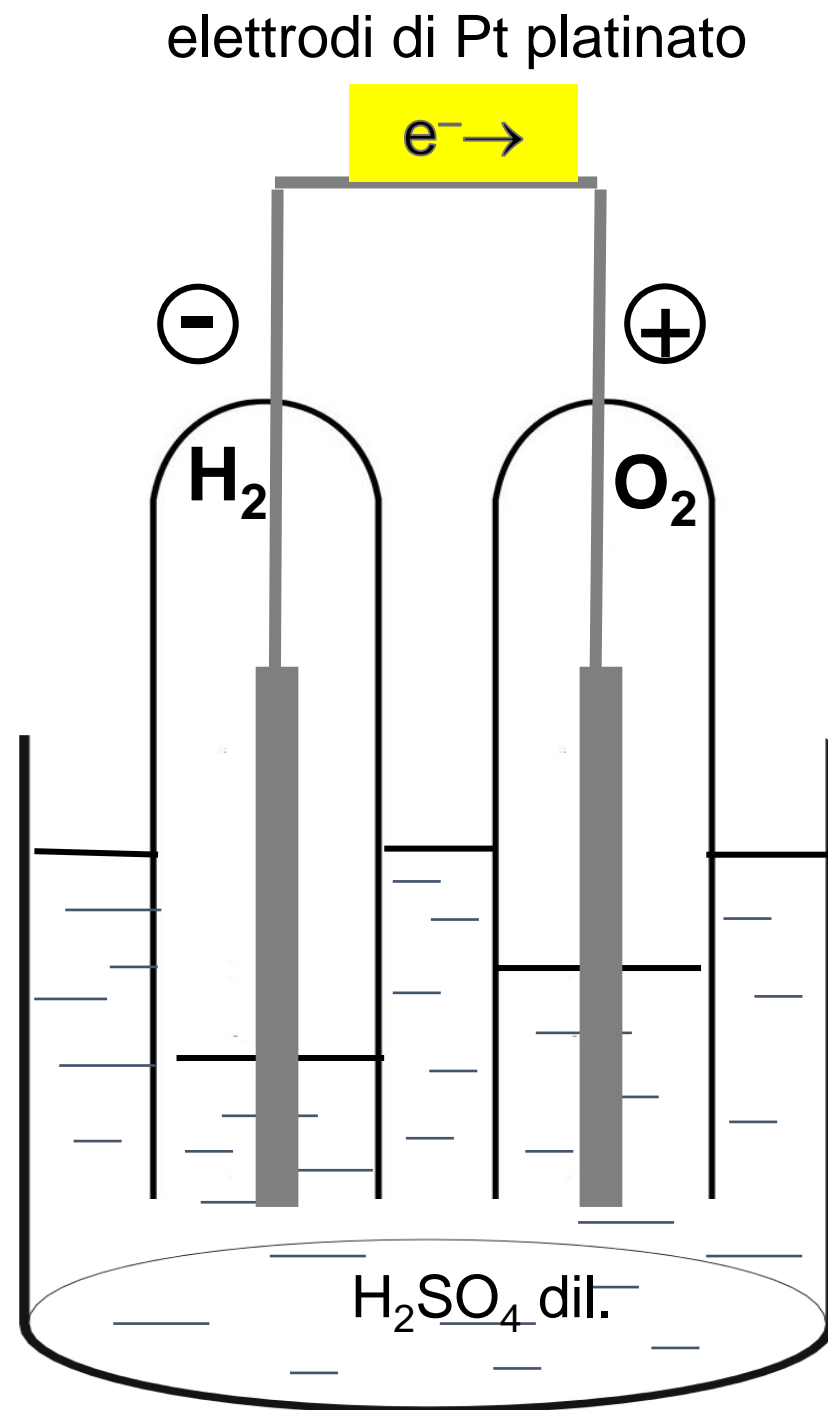
THE
LONDON, EDINBURGH AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

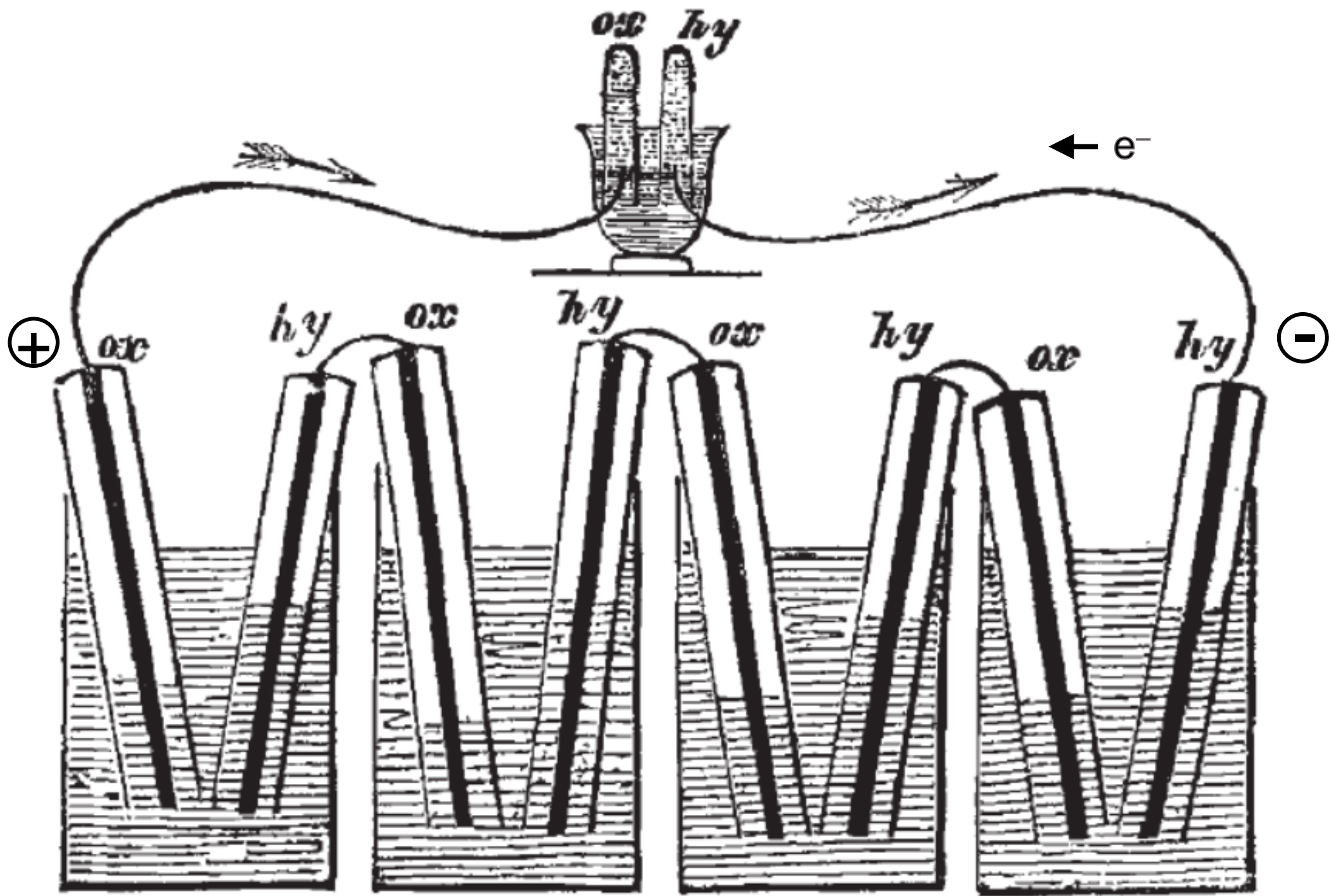
DECEMBER 1842.

LXXII. On a Gaseous Voltaic Battery. By W. R. GROVE,
Esq., M.A., F.R.S., Professor of Experimental Philosophy
in the London Institution.

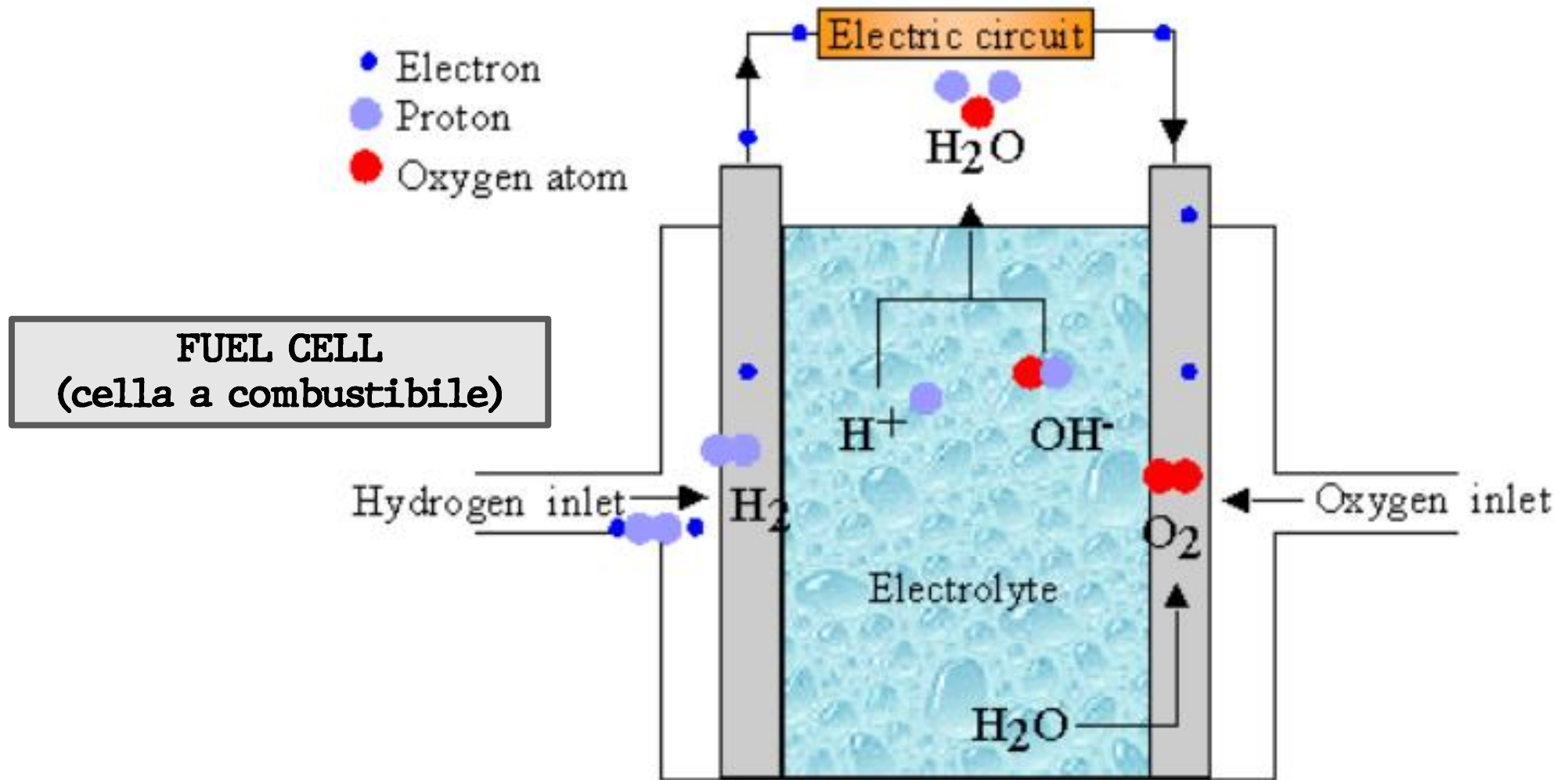


$$\Delta G^\circ = -n \times F \times \Delta E^\circ = -76 \text{ kcal mol}^{-1}$$





Una batteria Grove a 4 elementi, usata per fare l'elettrolisi dell'acqua



Electrolyte: NaOH aq, Sulfuric Acid, Phosphoric acid, Proton Exchange Membrane, Solid Polymer, Molten Carbonate & Solid Oxide

1889 Ludwig Mond e Charles Langer introducono il termine 'fuel cell'

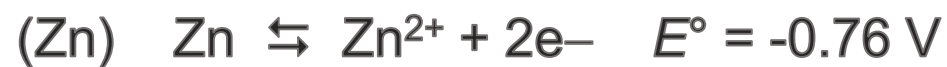
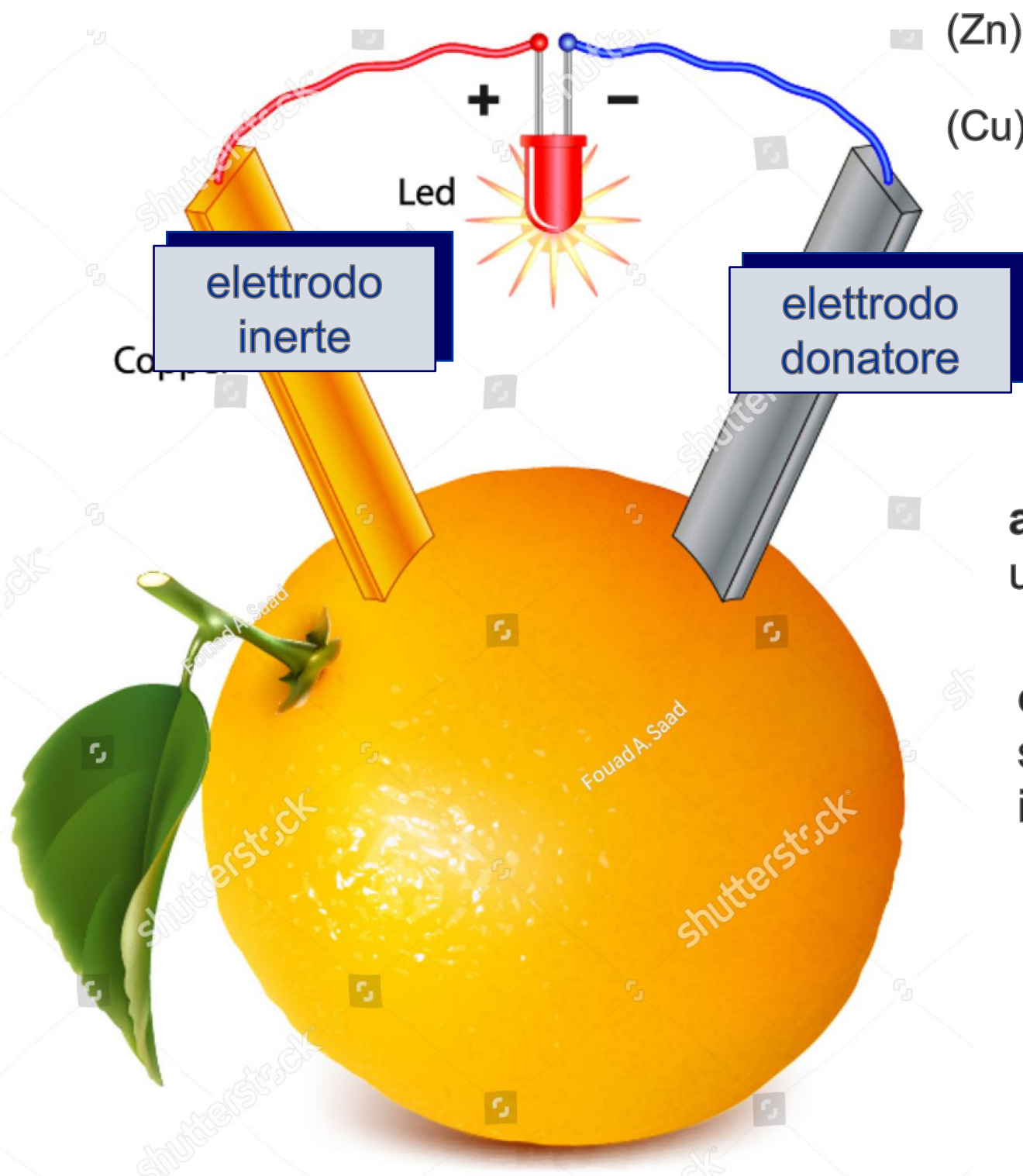
1932 prime applicazioni delle *fuel cells* (trattore a 20 HP)

1960 NASA, applicazioni aerospaziali

1970 Giappone, applicazioni nell'industria automobilistica

quasi quasi mi faccio una pila anch'io...

PILE ORTOFRUTTICOLE



anodo: elettrodo donatore \Rightarrow
un metallo con $E^\circ < 0.00 \text{ V}$

catodo: elettrodo inerte \Rightarrow un
supporto conduttore redox
inattivo (metallo, grafite)

SCUSA, PICCINA,
PERCHE' USI LA COPPIA
ZINCO-RAME?

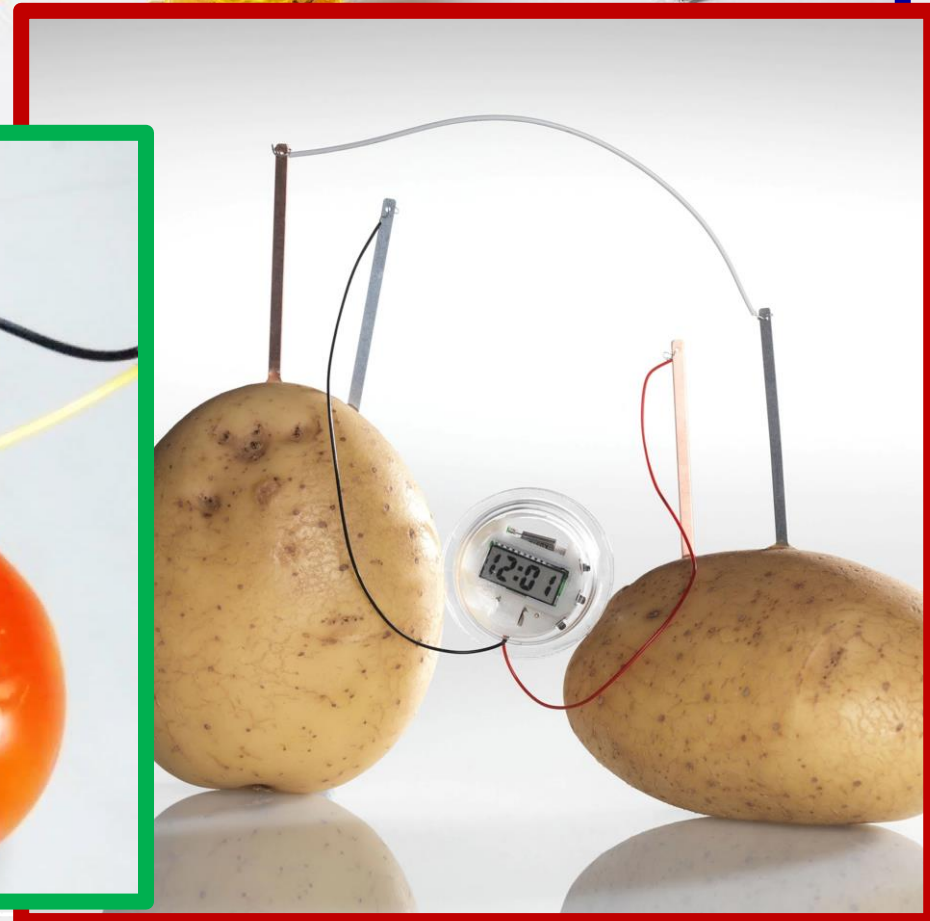
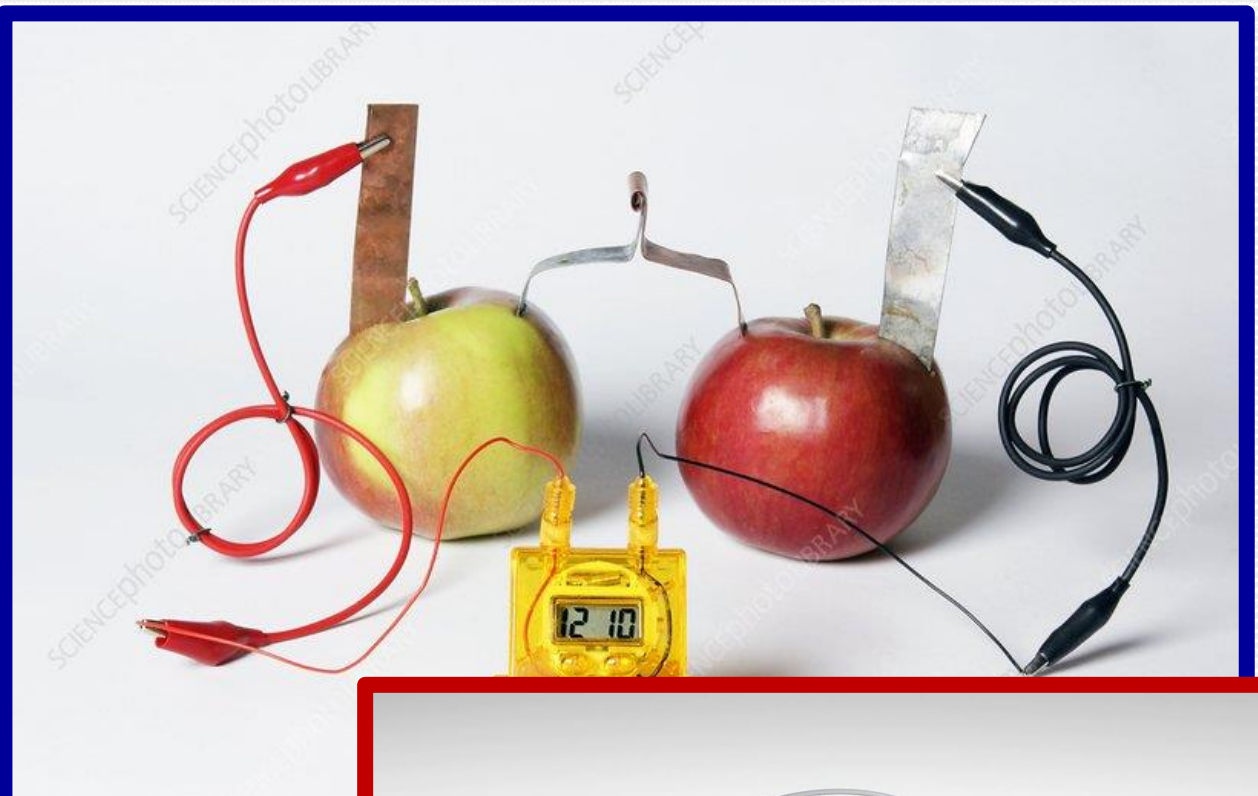
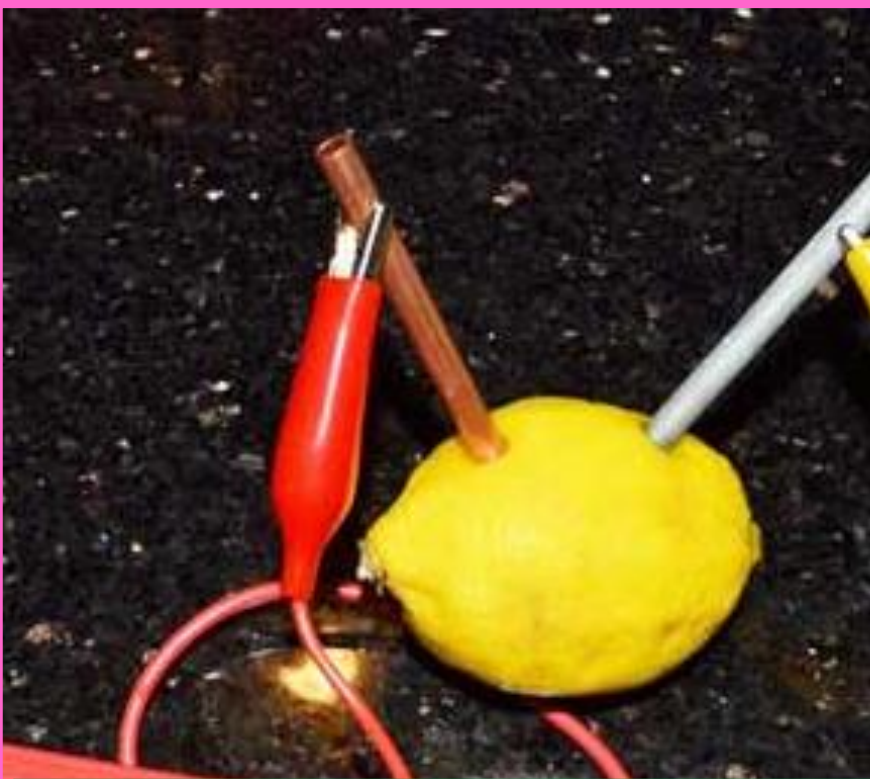
PERCHE' L'HA FATTO
ALESSANDRO VOLTA

Zn →
Cu →

12:00

ORTOFRUTTA

PILE ORTOFRUTTICOLE



**couronne de
tomates**

Pila all'arancia (Zn/Cu)

elettrodo
donatore
(Zn)

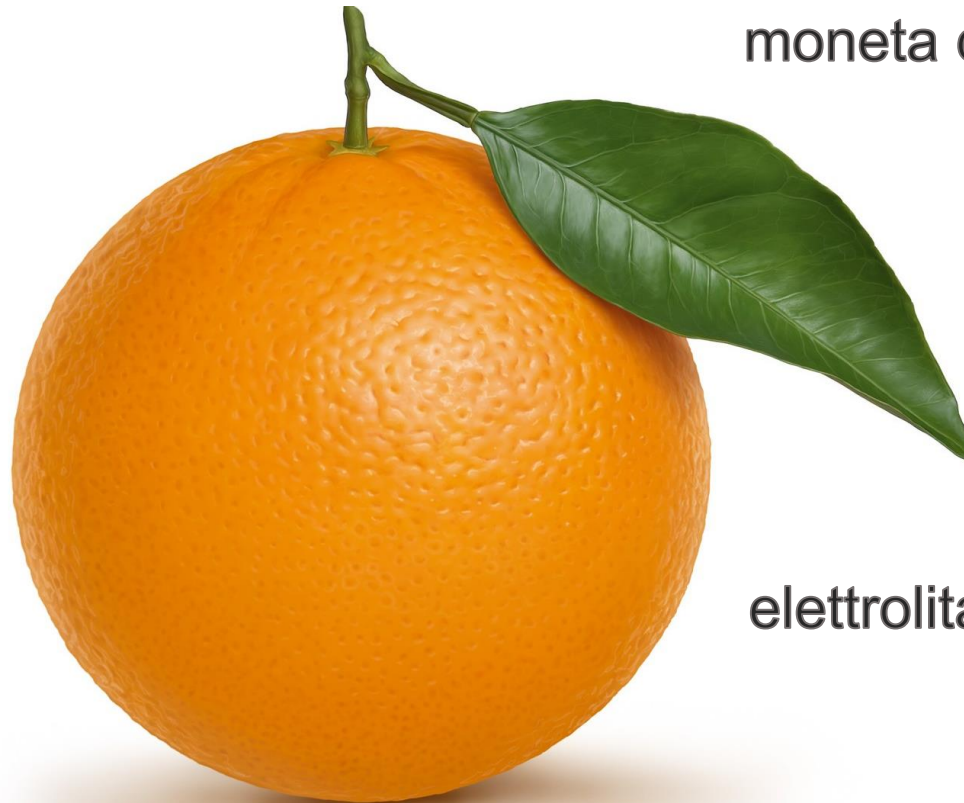


Fe zincato



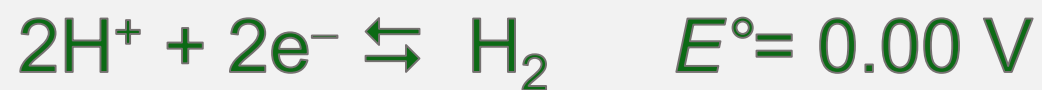
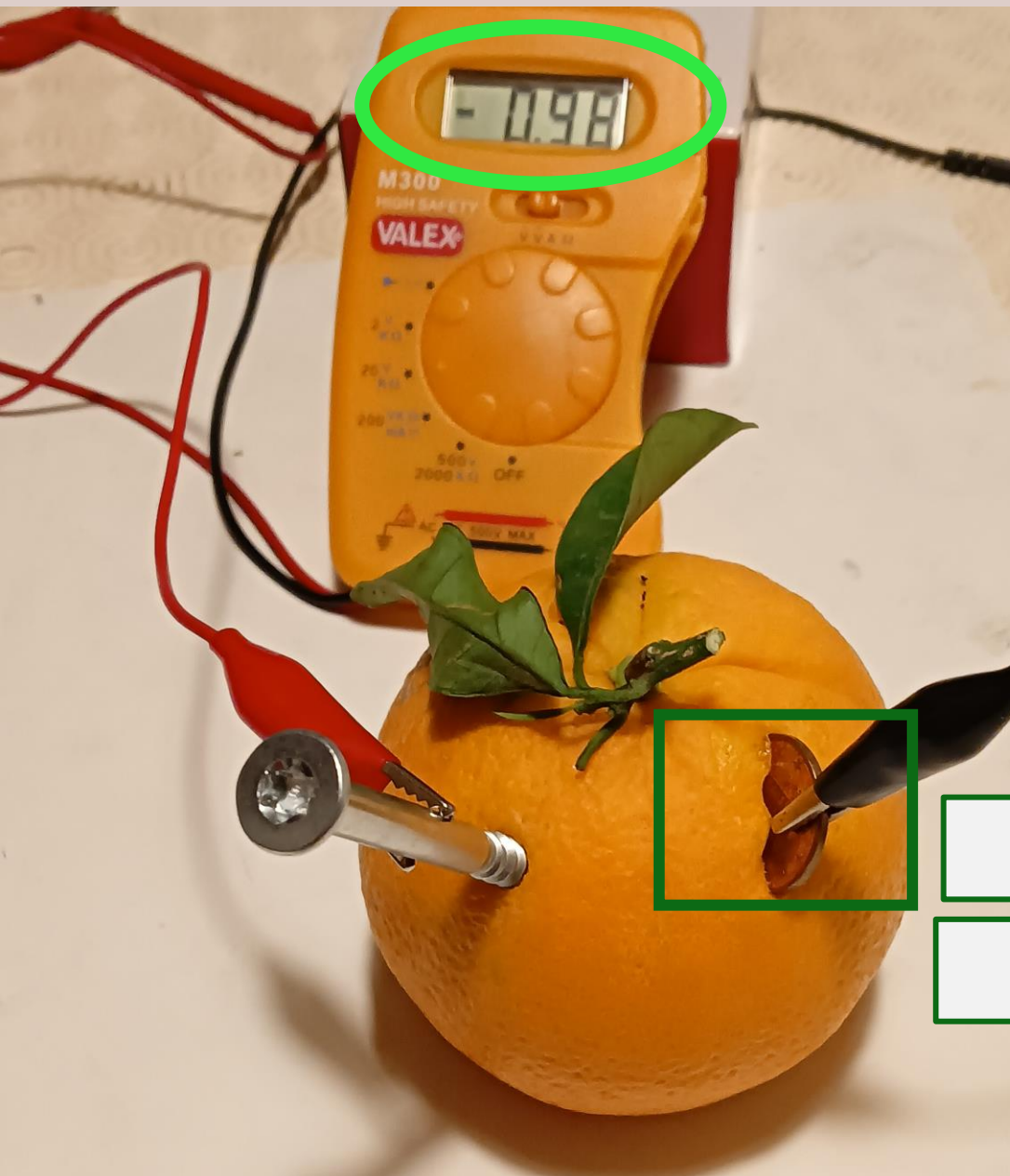
elettrodo
inerte
(Cu)

moneta da 5 cent



elettrolita

Esperimenti in cucina #1



$$\begin{aligned} \text{emf} &= 0.98 \text{ V} \\ \Delta E^{\circ} &= 0.76 \text{ V} \end{aligned}$$

Pila all'arancia (Zn/Fe_{inox})

elettrodo
donatore
(Zn)

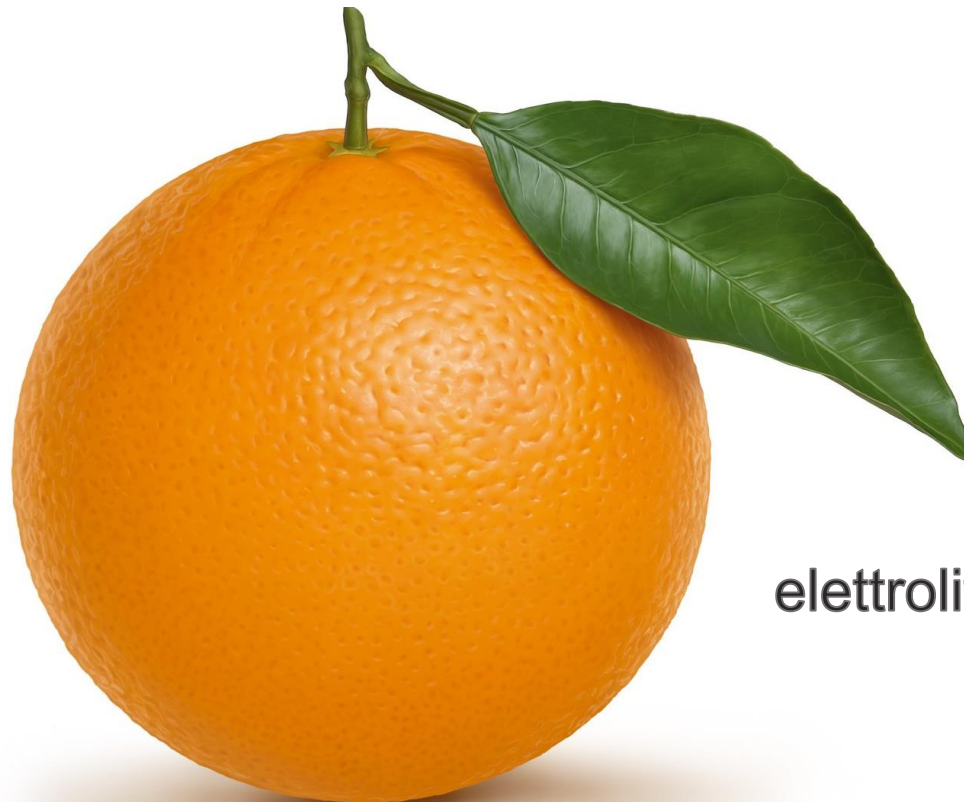


Fe zincato

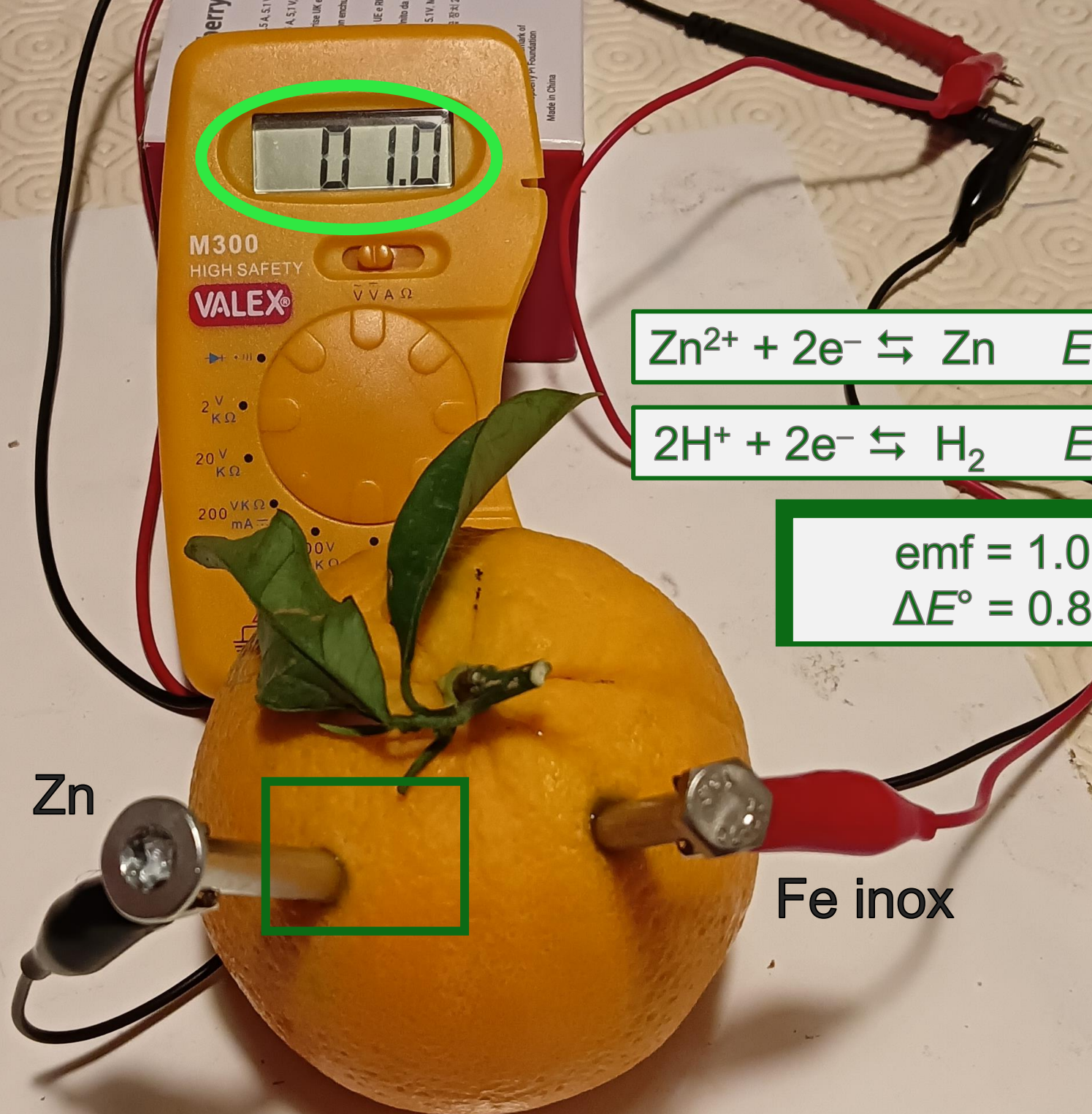
elettrodo
inerte



acciaio inox



elettrolita



emf = 1.0 V
 $\Delta E^{\circ} = 0.8 \text{ V}$

Zn

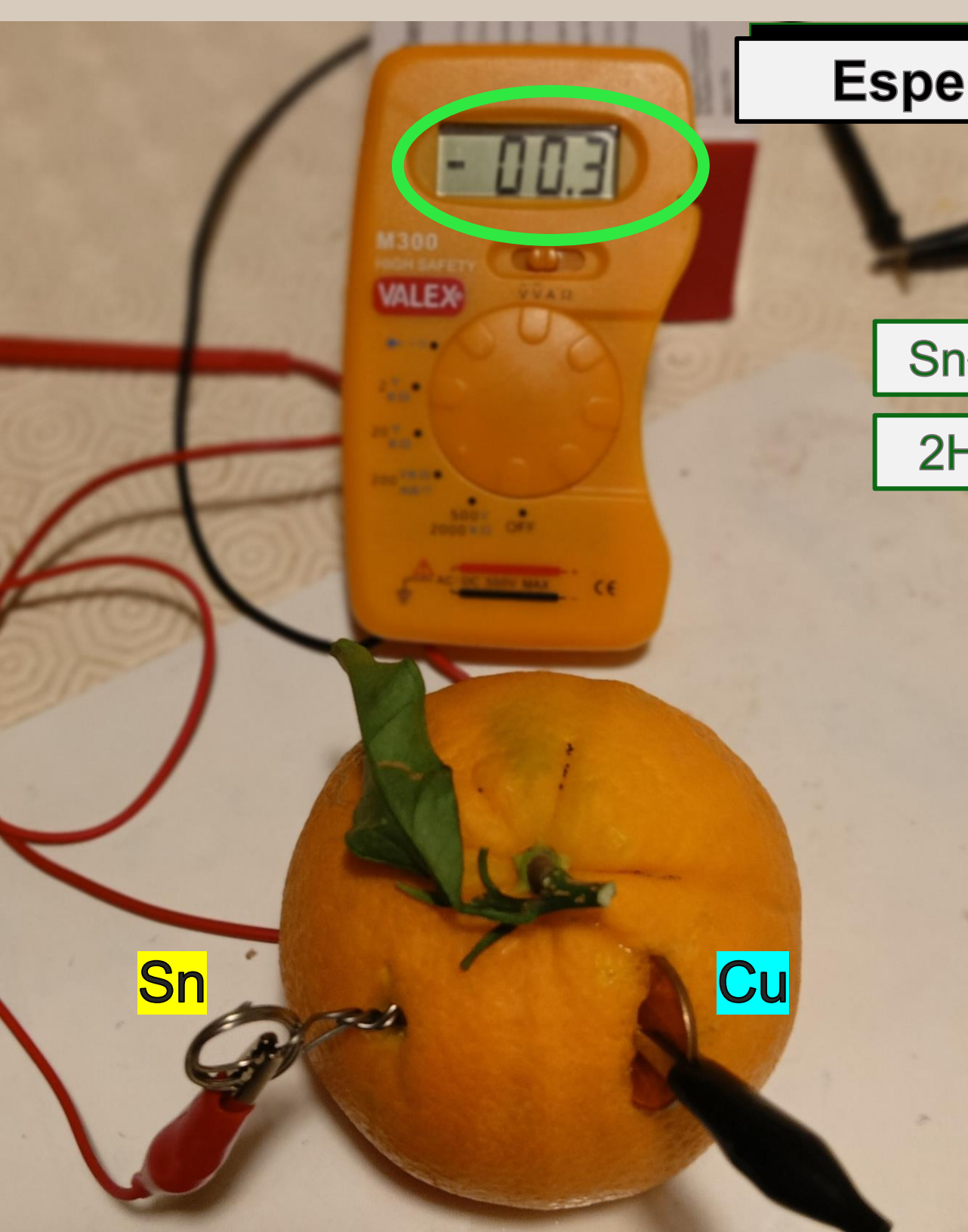
Fe inox

E perché non cambiare anche l'elettrodo donatore?
Basta che abbia $E^\circ < 0.00 \text{ V}$



stagno per saldatori
(4.50 €)

Esperimenti in cucina # 2



$$\text{emf} = 0.3 \text{ V}$$

$$\Delta E^{\circ} = 0.2 \text{ V}$$

Esperimenti in cucina # 3



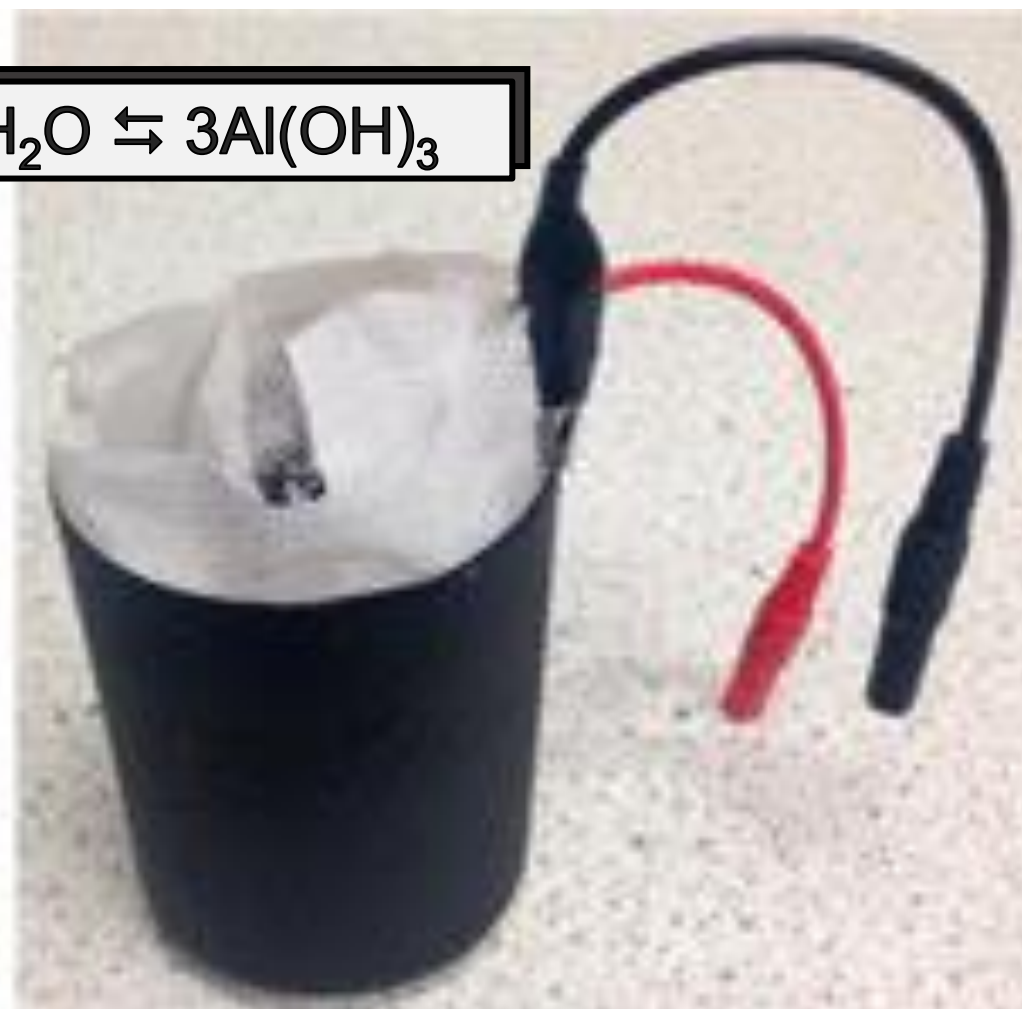
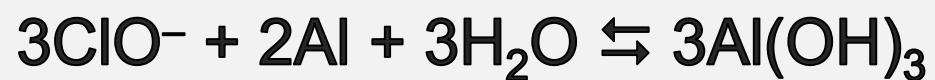
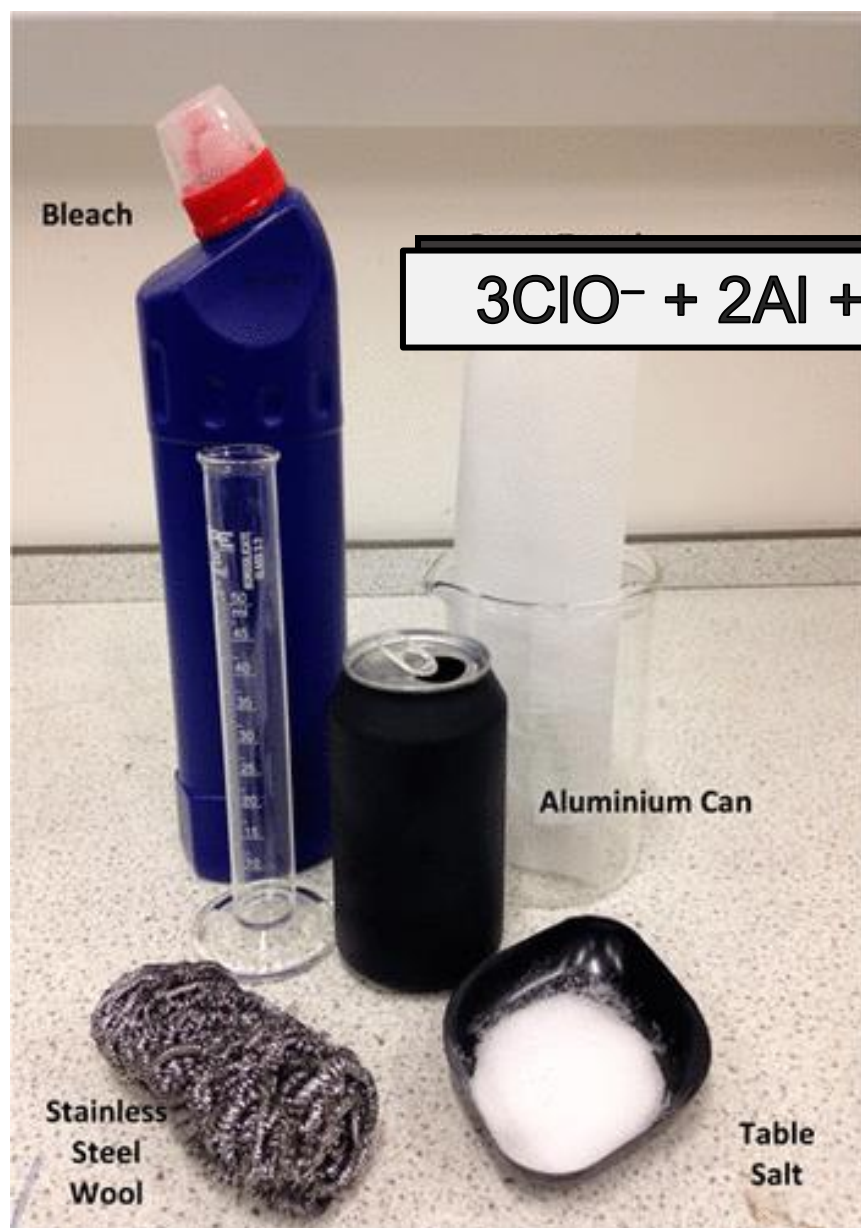
$$\text{emf} = 0.4 \text{ V}$$

$$\Delta E^{\circ} = 0.2 \text{ V}$$

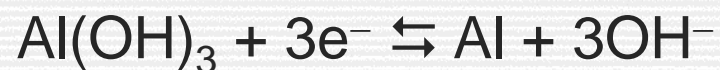
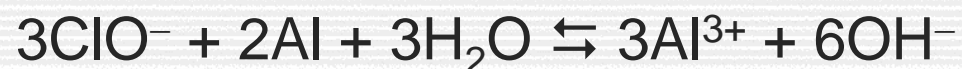
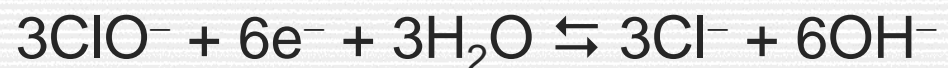
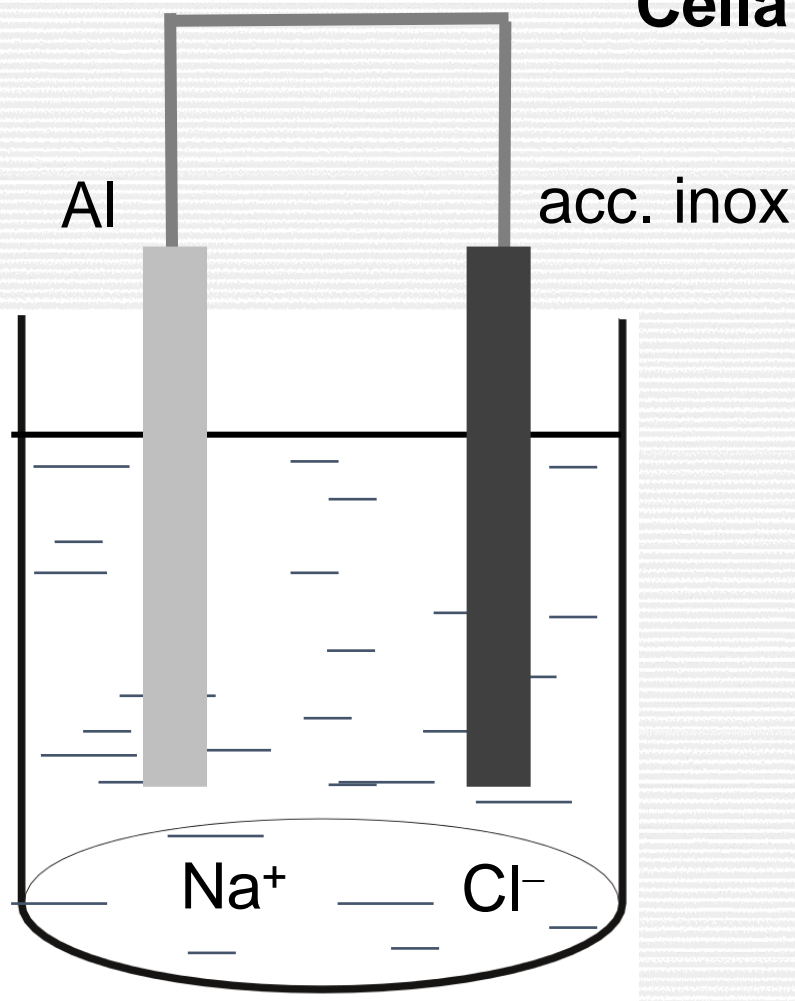
“Can” You Really Make a Battery Out of That?

Michael A. Parkes,^{*,†} Thomas Chen,[‡] Billy Wu,^{†,§} Vladimir Yufit,[†] and Gregory J. Offer^{†,§}

J. Chem. Educ. **2016**, 93, 681–686



Cella alluminio/ipoclorito – versione didattica



$$E^\circ = -2.31 \text{ V}$$

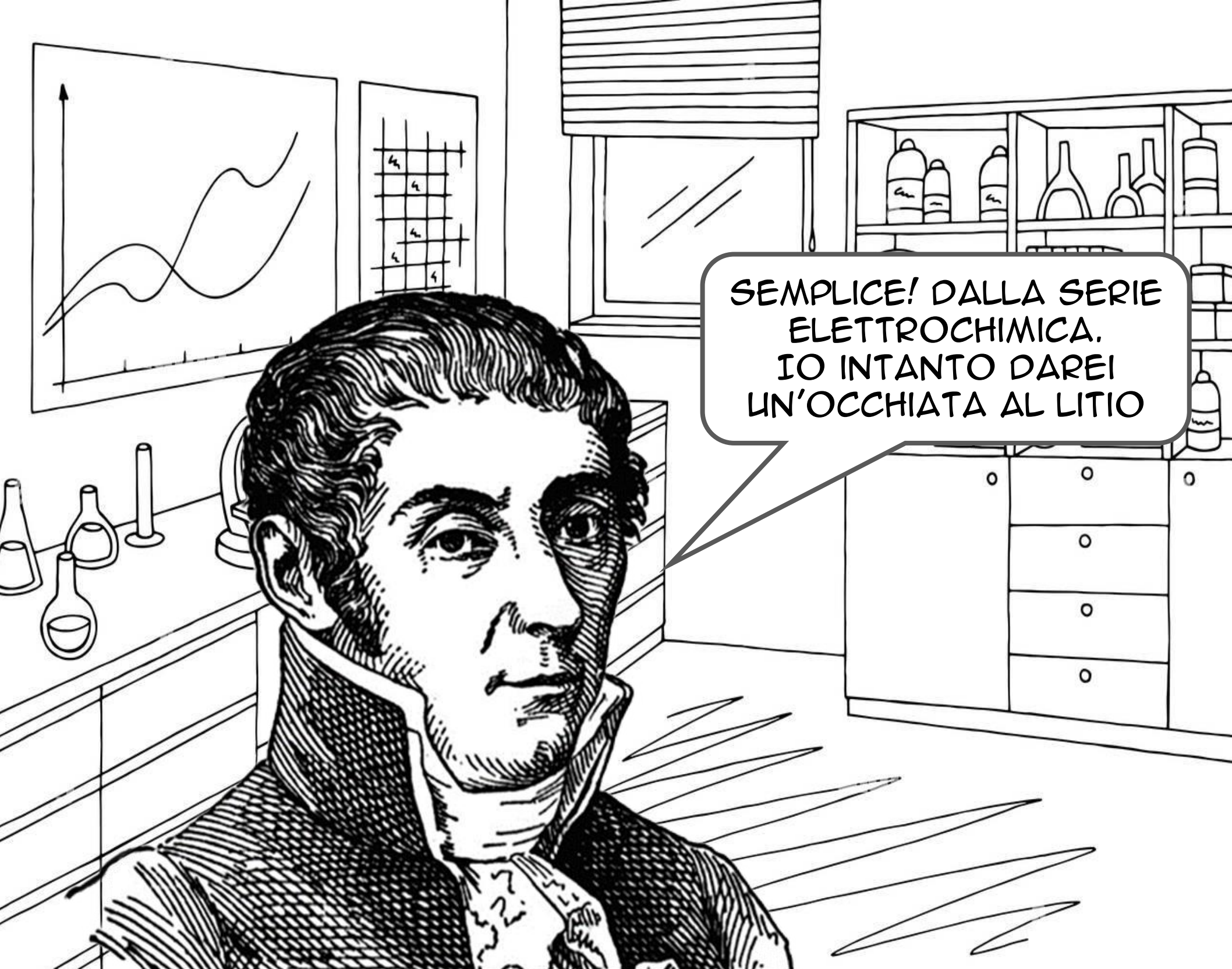


$$E^\circ = 0.89 \text{ V}$$

$$\Delta E^\circ = 3.20 \text{ V}$$

VORREI INVENTARE UNA
NUOVA BATTERIA, MA
NON SO DA DOVE
COMINCIARE





SEMPLICE! DALLA SERIE
ELETTROCHIMICA,
IO INTANTO DAREI
UN'OCCHIATA AL LITIO

TABLE 18.1

Standard Reduction Potentials at 25 °C

Reduction half-reaction	$E^\circ(\text{V})$
$\text{F}_2(\text{g}) + 2\text{e}^-$	2.87
$\text{Ce}^{4+}(\text{aq}) + \text{e}^-$	1.61
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\ell)$	1.51
$\text{Cl}_2(\text{g}) + 2\text{e}^-$	1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$	1.23
$\text{Br}_2(\ell) + 2\text{e}^-$	1.06
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^-$	0.96
$\text{Ag}^+(\text{aq}) + \text{e}^-$	0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^-$	0.77
$\text{I}_2(\text{s}) + 2\text{e}^-$	0.54
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$	0.34
$\text{AgCl}(\text{s}) + \text{e}^-$	0.222
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^-$	0.15
$2\text{H}^+(\text{aq}) + 2\text{e}^-$	0.000
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^-$	-0.126
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^-$	-0.25
$\text{Cr}^{3+}(\text{aq}) + \text{e}^-$	-0.41
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$	-0.76
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^-$	-1.57
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^-$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^-$	-2.714
$\text{Li}^+(\text{aq}) + \text{e}^-$	-3.045

semicella ossidante

ΔE°

semicella riducente

continua...