

# Accoppiamenti di semielementi per la formazione di pile

**Tabella** — Potenziali standard di semielementi in soluzione acquosa e a 25 °C, riferiti all'elettrodo standard di idrogeno (SHE; nota 25).

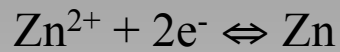
Semireazione	$E_0$ (V)	Semireazione	$E_0$ (V)
$Li^+ + e \rightleftharpoons Li$	-3,040	$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$	0,081
$K^+ + e \rightleftharpoons K$	-2,931	$S + 2H_3O^+ + 2e \rightleftharpoons H_2S + 2H_2O$	0,142
$Ca^{2+} + 2e \rightleftharpoons Ca$	-2,868	$Sn^{4+} + 2e \rightleftharpoons Sn^{2+} (HCl\ 1F)$	0,151
$Na^+ + e \rightleftharpoons Na$	-2,7109	$Cu^{+2} + e \rightleftharpoons Cu^+$	0,153
$Mg^{2+} + 2e \rightleftharpoons Mg$	-2,372	$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$	0,2681
$H_3O^+ + e \rightleftharpoons H_2O + H$	-2,10	$Cu^{2+} + 2e \rightleftharpoons Cu$	0,342
$Al^{3+} + 3e \rightleftharpoons Al$	-1,662	$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$	0,401
$Ti^{2+} + 2e \rightleftharpoons Ti$	-1,630	$Cu^+ + e \rightleftharpoons Cu$	0,521
$ZnO_2^{2-} + 2H_2O + 2e \rightleftharpoons Zn + 4OH^-$	-1,215	$I_2 + 2e \rightleftharpoons 2I^-$	0,535
$Mn^{2+} + 2e \rightleftharpoons Mn$	-1,185	$O_2 + 2H_3O^+ + 2e \rightleftharpoons H_2O_2 + 2H_2O$	0,682
$Cr^{2+} + 2e \rightleftharpoons Cr$	-0,913	$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	0,771
$2H_2O + 2e \rightleftharpoons H_2 + 2OH^-$	-0,8277	$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	0,7973
$Te + 2H_3O^+ + 2e \rightleftharpoons H_2Te + 2H_2O$	-0,783	$Ag^+ + e \rightleftharpoons Ag$	0,7996
$Zn^{2+} + 2e \rightleftharpoons Zn$	-0,7618	$2NO_3^- + 4H_3O^+ + 2e \rightleftharpoons N_2O_4 + 6H_2O$	0,803
$Cr^{3+} + 3e \rightleftharpoons Cr$	-0,744	$NO_3^- + 3H_3O^+ + 2e \rightleftharpoons HNO_2 + 4H_2O$	0,934
$As + 3H_3O^+ + 3e \rightleftharpoons AsH_3 + 3H_2O$	-0,608	$NO_3^- + 4H_3O^+ + 3e \rightleftharpoons NO + 6H_2O$	0,957
$H_3PO_2 + H_3O^+ + e \rightleftharpoons P + 3H_2O$	-0,508	$Br_{2(l)} + 2e \rightleftharpoons 2Br^-$	1,065
$Fe^{2+} + 2e \rightleftharpoons Fe$	-0,447	$Pt^{2+} + 2e \rightleftharpoons Pt$	1,118
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$	-0,407	$MnO_2 + 4H_3O^+ + 2e \rightleftharpoons Mn^{2+} + 6H_2O$	1,224
$Cd^{2+} + 2e \rightleftharpoons Cd$	-0,403	$O_2 + 4H_3O^+ + 4e \rightleftharpoons 6H_2O$	1,229
$Se + 2H_3O^+ + 2e \rightleftharpoons H_2Se + 2H_2O$	-0,400	$Cr_2O_7^{2-} + 14H_3O^+ + 6e \rightleftharpoons 2Cr^{3+} + 21H_2O$	1,232
$Tl^+ + e \rightleftharpoons Tl$	-0,336	$Cl_2 + 2e \rightleftharpoons 2Cl^-$	1,358
$Co^{2+} + 2e \rightleftharpoons Co$	-0,277	$ClO_3^- + 6H_3O^+ + 6e \rightleftharpoons Cl^- + 9H_2O$	1,451
$Ni^{2+} + 2e \rightleftharpoons Ni$	-0,257	$PbO_2 + 4H_3O^+ + 2e \rightleftharpoons Pb^{2+} + 6H_2O$	1,455
$Mo^{3+} + 3e \rightleftharpoons Mo$	-0,200	$MnO_4^- + 8H_3O^+ + 5e \rightleftharpoons Mn^{2+} + 12H_2O$	1,507
$Sn^{2+} + 2e \rightleftharpoons Sn$	-0,1374	$HClO + H_3O^+ + e \rightleftharpoons \frac{1}{2}Cl_2 + 2H_2O$	1,611
$Pb^{2+} + 2e \rightleftharpoons Pb$	-0,1263	$H_2O_2 + 2H_3O^+ + 2e \rightleftharpoons 4H_2O$	1,776
$2H_3O^+ + 2e \rightleftharpoons H_2 + 2H_2O$	0	$Co^{3+} + e \rightleftharpoons Co^{2+} (H_2SO_4\ 2F)$	1,83
$NO_3^- + H_2O + 2e \rightleftharpoons NO_2^- + 2OH^-$	0,01	$F_2 + 2e \rightleftharpoons 2F^-$	2,866

# Le Pile chimiche

- Ogni volta che si accoppiano due elettrodi qualsiasi, tra quelli che abbiamo visto sopra (nella tabella dei potenziali standard), si ottiene un dispositivo in grado di sfruttare la differenza di potenziale ai capi dei due elettrodi per generare corrente elettrica continua. Questo dispositivo si dice pila ed è in grado di trasformare l'energia chimica in energia elettrica.
  - ▶ Pile primarie
  - ▶ Pile secondarie (accumulatori)

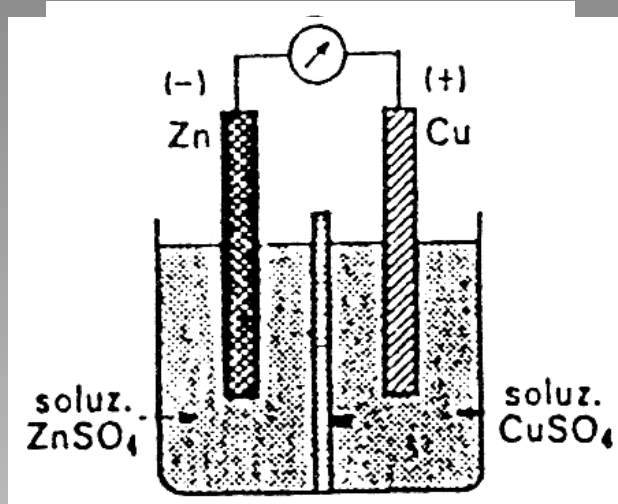
# Esempio 1

Equilibrio elettrodico

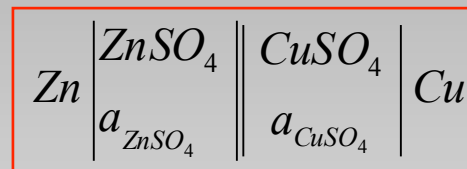


Potenziale elettrodico

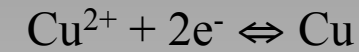
$$E_{(-)} = E_{\text{Zn}^{2+}/\text{Zn}}^o + \frac{0.0591}{2} \log \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}}$$



Schematizzazione della cella



Equilibrio elettrodico



Potenziale elettrodico

$$E_{(+)} = E_{\text{Cu}^{2+}/\text{Cu}}^o + \frac{0.0591}{2} \log \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}}}$$

$$\text{f.e.m.} = E_{(+)} - E_{(-)}$$

$$\text{f.e.m.} = \left( E_{\text{Cu}^{2+}/\text{Cu}}^o + \frac{0.0591}{2} \log a_{\text{Cu}^{2+}} \right) - \left( E_{\text{Zn}^{2+}/\text{Zn}}^o + \frac{0.0591}{2} \log a_{\text{Zn}^{2+}} \right)$$

$$\text{f.e.m.} = \left( E_{\text{Cu}^{2+}/\text{Cu}}^o - E_{\text{Zn}^{2+}/\text{Zn}}^o \right) + \frac{0.0591}{2} \log \frac{a_{\text{Cu}^{2+}}}{a_{\text{Zn}^{2+}}}$$

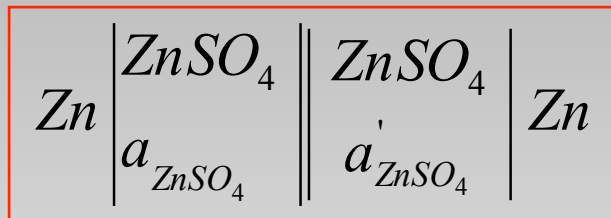
# Pile a concentrazione

La f.e.m. di una pila è data dalla differenza di potenziale tra due elettrodi;

si dicono **pile chimiche** quando i due elettrodi sono diversi cioè su di essi avvengono due diverse reazioni elettrodiche;

si dicono **pile a concentrazione** quando i due elettrodi sono uguali cioè sui due elettrodi avviene la stessa reazione elettrodica.

## Esempio 1



In cui  $a \neq a'$  ; supponiamo che  $a' > a$

Equilibrio elettrodico



Potenziale elettrodico

$$E = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}}$$

$$\text{f.e.m.} = E_{(+)} - E_{(-)}$$

$$\text{f.e.m.} = \left( E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log a'_{\text{Zn}^{2+}} \right) - \left( E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log a_{\text{Zn}^{2+}} \right)$$

$$\text{f.e.m.} = \frac{0.0591}{2} \log \frac{a'_{\text{Zn}^{2+}}}{a_{\text{Zn}^{2+}}}$$

# Legge di Faraday

Faraday fu il primo a stabilire una relazione quantitativa tra le quantità di specie elettrochimicamente attive, reagenti e prodotte, in una reazione di ossidoriduzione con la quantità di corrente che circola nel circuito esterno.

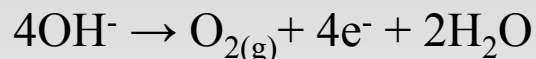
Infatti per la reazione  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$  si può osservare che la formazione di una mole di Ag metallico (108.0 g) è legato al passaggio nel circuito di una quantità di carica elettrica pari ad 1.0 mole di elettroni.

Questa quantità di carica, detta costante di Faraday, è pari a:

| carica di un elettrone | \* Numero di Avogadro

$$1.6022 \cdot 10^{-19} * 6.0221694 \cdot 10^{23} = 96485 \text{ Coulomb}$$

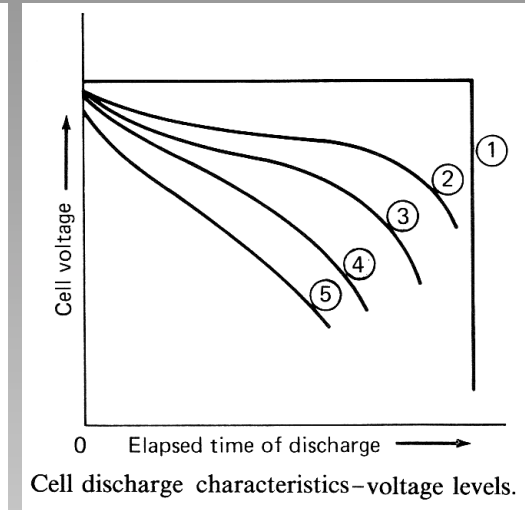
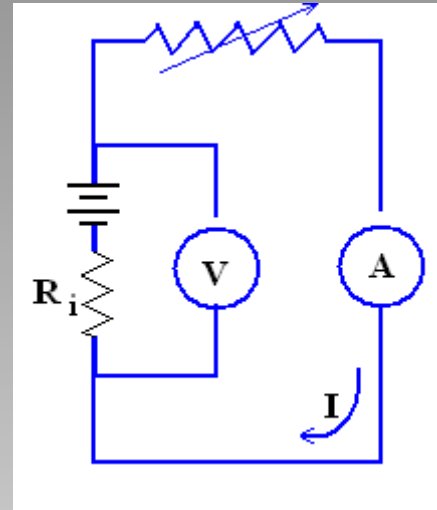
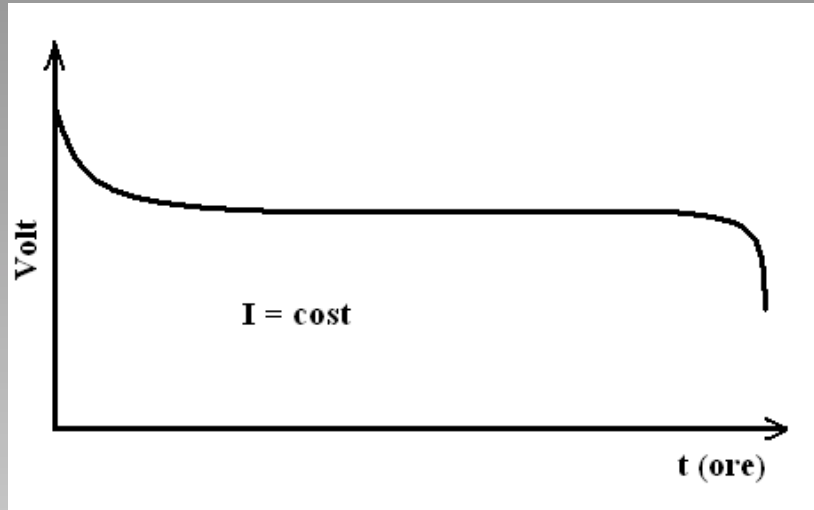
Se la stessa quantità di carica elettrica venisse utilizzata nella di riduzione dello zinco  $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$  si avrebbe la formazione di mezza mole di Zn ( $65.39/2 = 32.695$  g); ed ancora se venisse utilizzata nell'ossidazione dell'  $\text{OH}^-$  secondo la reazione:



si avrebbe la formazione di  $\frac{1}{4}$  di mole di ossigeno molecolare gassoso ( $32/4 = 8$  g).

**Faraday si esprime dicendo che: al passaggio di un equivalente di corrente si ha la formazione o il consumo di un equivalente di sostanza elettrochimicamente attiva.**

$$V = E - IR_i - (\eta_a - |\eta_c|)$$



### Caratteristiche di merito

Capacità specifica Ah/kg

Energia specifica Wh/kg

Densità di energia Wh/cm<sup>3</sup>

Potenza specifica W/kg

$$\text{Cap}_{sp} \cdot V = \text{Energia}_{sp}$$

$$I = \frac{C_n}{N}$$

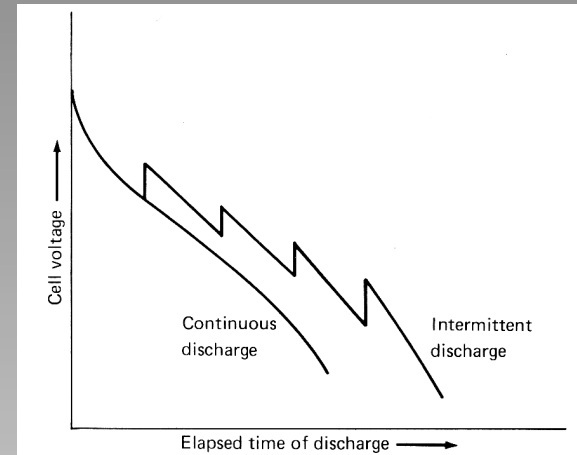
Dove I = corrente di scarica (A)

$C_n$  = Tasso di Capacità della cella ad un regime di n-ore di scarica

N = ore di scarica

# Tipi di scarica:

continua o ad intermittenza

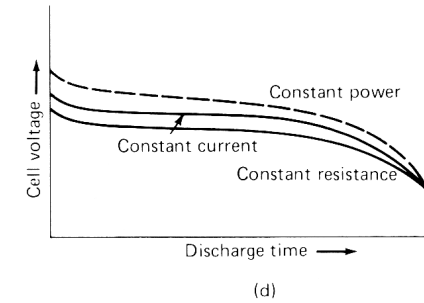
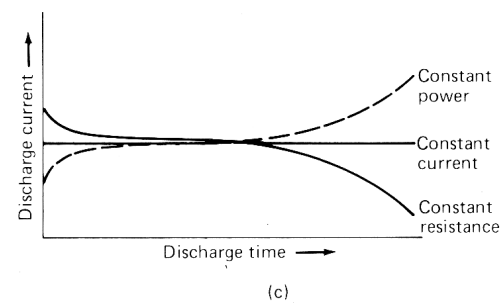
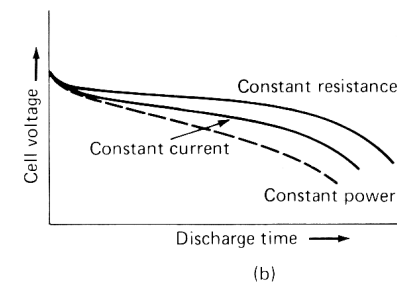
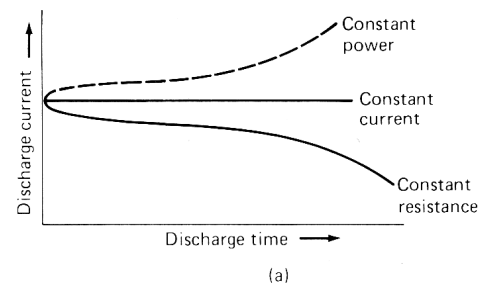


Effect of intermittent discharge on battery capacity.

A corrente costante

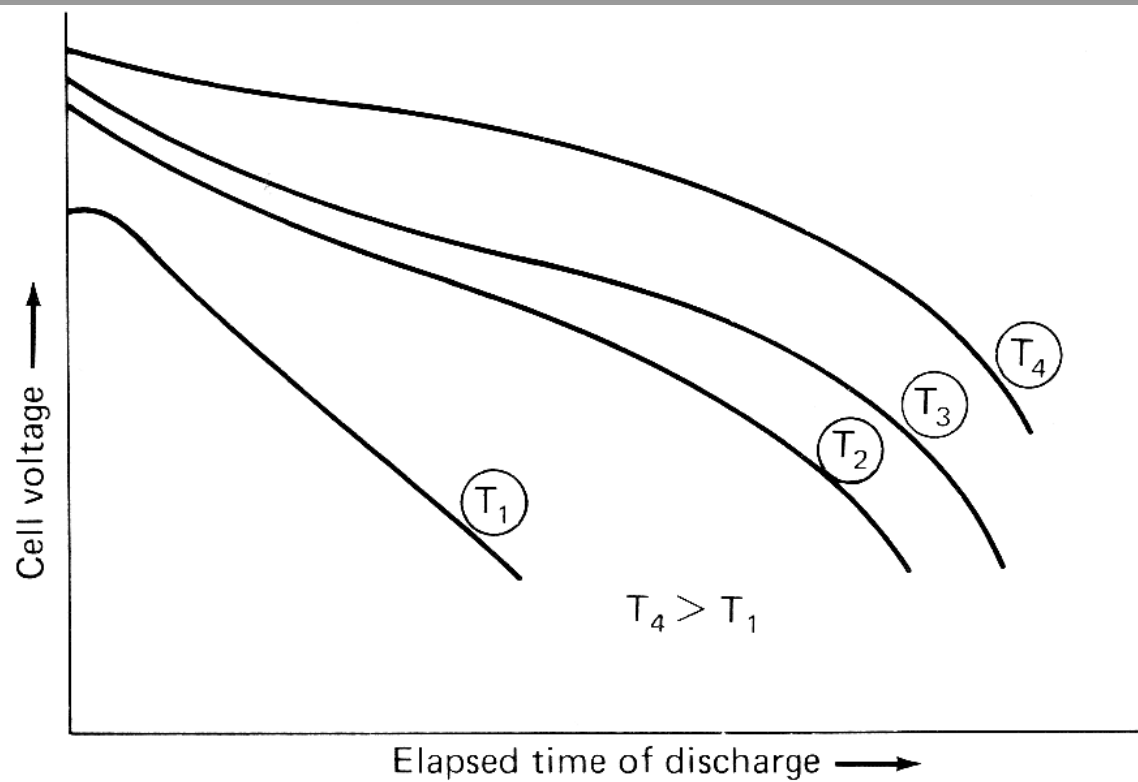
A carico costante

A potenza costante



Discharge profiles under different discharge modes. (a) Current profile (same starting current); (b) voltage profile (same starting current); (c) current profile (same average current); (d) voltage profile (same average current).

## Effetto della temperatura sulla scarica



Effect of temperature on battery capacity. ( $T_1$  to  $T_4$  represent increasing temperature.)



**TABLE IEC Designation and Dimensions of Round Cells and Batteries\***

Designation		Nominal cell dimensions, mm		Maximum battery, dimensions, mm		Approx. weight, kg
IEC	ANSI	Diameter	Height	Diameter	Height	
R 08		...	...	11.6	3.5	
R 06		10	22	...	...	
R 03	AAA	...	...	10.5	44.5	8.2
R 01		...	...	12.0	14.7	
R 0		11	19	...	...	
R 1	N	...	...	12.0	30.2	
R 3		13.5	25	...	...	
R 4	R	13.5	38	...	...	10.4
R 6	AA	...	...	14.5	50.5	15
R 8	A	16	47.8	...	...	21
R 9		...	...	16.0	6.2	
R 10		...	...	21.8	37.3	
R 12	B	...	...	21.5	60.0	35
R 14	C	...	...	26.2	50.0	45
R 15		24	70	...	...	
R 17		25.5	17	...	...	
R 18		25.5	83	...	...	
R 19		32	17	...	...	
R 20	D	...	...	34.2	61.5	100
R 22	E	32	75	...	...	132
R 25	F	32	91	...	...	159
R 26	G	32	105	...	...	181
R 27	J	32	150	...	...	272
R 40	6	...	...	67.0	172.0	998
R 41		...	...	7.9	3.6	
R 42		...	...	11.6	3.6	
R 43		...	...	11.6	4.2	
R 44		...	...	11.6	5.4	
R 45		...	...	9.5	3.6	
R 48		...	...	7.9	5.4	
R 50		...	...	16.4	16.8	
R 51		...	...	16.5	50.0	
R 52		...	...	16.4	11.4	
R 53		...	...	23.2	6.1	

\*Where a single-cell battery is specified, the maximum dimensions are given instead of nominal dimensions; weight is approximate, not specified in standards.

SOURCE: International Electrotechnical Commission (IEC Standard)<sup>2</sup> and American National Standards Institute C 18.1 (1965).

ministilo

stilo

torcia

torcione

**TABLE** Characteristics of Electrode Materials\*

Material	Atomic or molecular weight, g	Standard reduction potential at 25°C, V	Valence change	Melting point, °C	Density, g/cm <sup>3</sup>	Electrochemical equivalents		
						Ah/g	g/Ah	Ah/cm <sup>3</sup> ‡
Anode materials								
H <sub>2</sub>	2.01	0	2	—	—	26.59	0.037	
Li	6.94	-3.01	1	180	0.54	3.86	0.259	2.06
Na	23.0	-2.71	1	98	0.97	1.16	0.858	1.14
Mg	24.3	-2.38 -2.69†	2	650	1.74	2.20	0.454	3.8
Al	26.9	-1.66	3	659	2.69	2.98	0.335	8.1
Ca	40.1	-2.84 -2.35†	2	851	1.54	1.34	0.748	2.06
Fe	55.8	-0.44	2	1528	7.85	0.96	1.04	7.5
Zn	65.4	-0.76 -1.25†	2	419	7.14	0.82	1.22	5.8
Cd	112.4	-0.40	2	321	8.65	0.48	2.10	4.1
Pb	207.2	-0.13	2	327	11.34	0.26	3.87	2.9
Cathode materials								
O <sub>2</sub>	32.0	1.23	4	—	—	3.35	0.30	
Cl <sub>2</sub>	71.0	1.36	2	—	—	0.756	1.32	
SO <sub>2</sub>	64.0	—	1	—	—	0.419	2.38	
MnO <sub>2</sub>	86.9	1.23‡	1	—	5.0	0.308	3.24	1.54
NiOOH	91.7	0.49†	1	—	7.4	0.292	3.42	2.16
CuCl	99.0	0.14	1	—	3.5	0.270	3.69	0.95
FeS <sub>2</sub>	119.9	—	4	—	—	0.89	1.12	4.35
AgO	123.8	0.57†	2	—	7.4	0.432	2.31	3.20
Br <sub>2</sub>	159.8	1.07	2	—	—	0.385	2.95	
HgO	216.6	0.10†	2	—	11.1	0.247	4.05	2.74
Ag <sub>2</sub> O	231.7	0.35†	2	—	7.1	0.231	4.33	1.64
PbO <sub>2</sub>	239.2	1.69	2	—	9.4	0.224	4.45	2.11

\* See also Appendixes B and C and Table 14.4.

† Basic electrolyte; all others, aqueous acid electrolyte.

‡ Based on density values shown.

# Confronto di batterie primarie

**TABLE** Comparison of Primary Batteries (Cylindrical Cells)

	Zinc-carbon (standard)	Zinc-carbon (heavy-duty ZnCl <sub>2</sub> )	Zn/MnO <sub>2</sub> (alkaline)	Zn/HgO	Mg/MnO <sub>2</sub>	Li/SO <sub>2</sub>	Li/SOCl <sub>2</sub> (bobbin type)	Li/MnO <sub>2</sub>	Li/CuO	Secondary cells	
										Sealed Pb-acid	Sealed Ni-Cd
Working voltage, V	1.2	1.2	1.2	1.25	1.75	2.8	3.3	2.8	1.5	2.0	1.2
D-size cells (54 cm <sup>3</sup> )											
Ah	4.5	6	10	14	7	8	10.2			2.7	3.5
Wh	5.4	7.2	12	17.5	12.2	22.4	34			5.4	4.3
Weight, g	85	93	125	165	105	85	100			180	140
Wh/kg	65	75	95	105	115	260	340			30	31
Wh/L	100	135	220	325	225	415	675			100	80
N-size cells (3.0 cm <sup>3</sup> )											
Ah	0.42		0.65		0.5				1.0*		
Wh	0.5		0.78		0.87				2.8		
Weight, g	6.3		9.5		5.0				13		
Wh/kg	75		80		170				215		
Wh/L	160		260		290				410		
AA-size cells (7.7 cm <sup>3</sup> )											
Ah	1.0		1.7			1.0	1.6		3.4		0.5
Wh	1.2		2.0			2.8	5.2		5.0		0.6
Weight, g	14.7		23			14	19		17.4		28
Wh/kg	80		86			200	275		275		2
Wh/L	170		250			360	670		650		200

\*2N size.

## Confronto di batterie primarie

**TABLE** Comparison of Primary Batteries (Button Cells)

Size: "44" IEC, 1154; 11.6 mm diam.  $\times$  5.4 mm high; volume: 0.55 cm<sup>3</sup>.

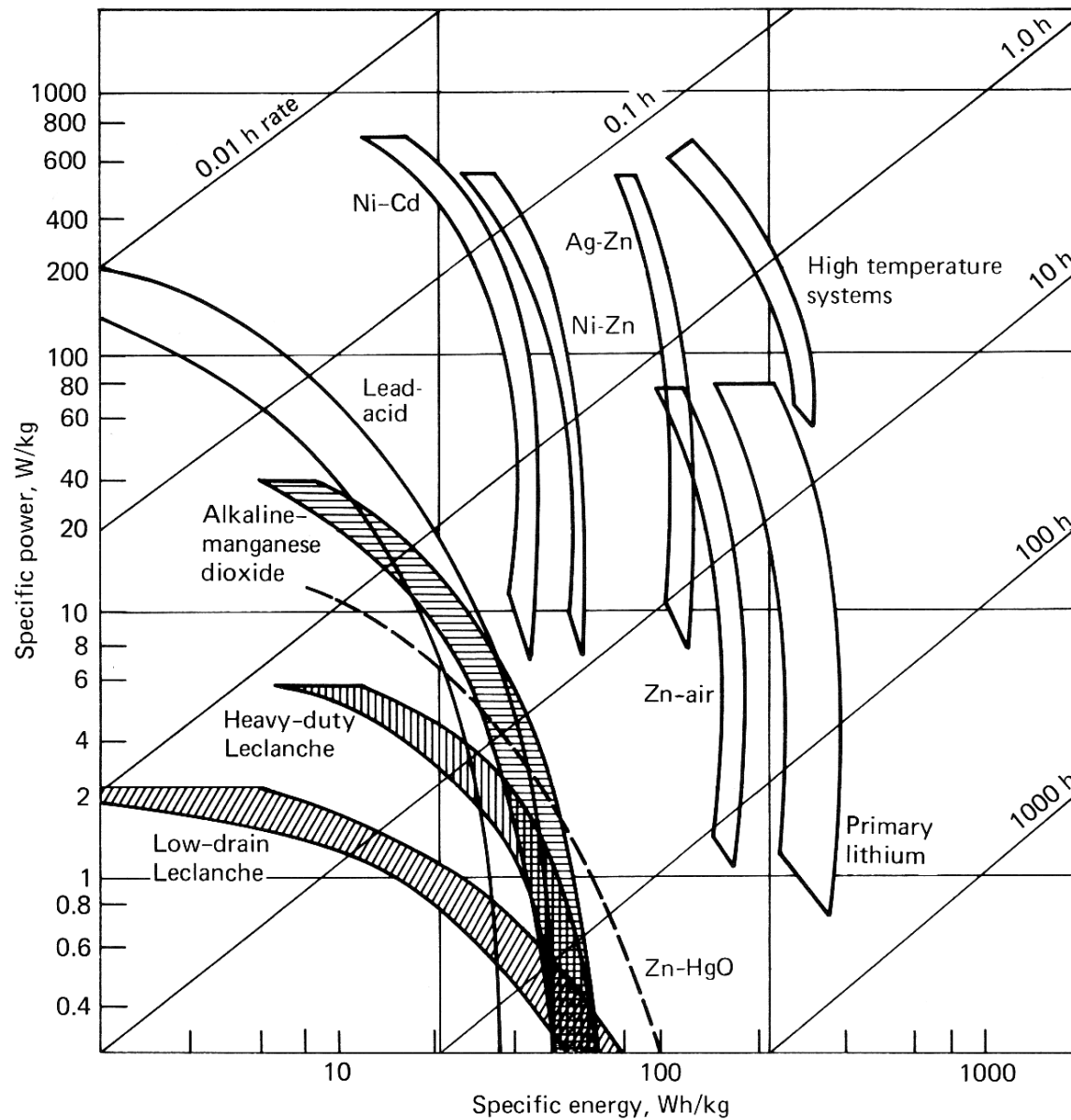
System	Voltage, V		Capacity*		Weight, g	Energy density*	
	Nominal	Working	mAh	mWh		mWh/g	Wh/L
Zn/alk/MnO <sub>2</sub>	1.5	1.25	60	75	2.0	37.5	135
Zn/HgO	1.35	1.3	180–230	260	2.6	100	470
Zn/Ag <sub>2</sub> O	1.5	1.55	175–200	285	2.2	130	515
Zn/AgO	1.5	1.55	245	380	2.2	170	690
Zn/air	1.25	1.25	400	500	1.7	290	905
Li/FeS <sup>†</sup>	1.5	1.4	100	140	1.1	125	370
Li/FeS <sub>2</sub>	1.5	1.4	160	220	1.7	130	400
Li/CuO	1.5	1.4	225	315	1.7	135	570
Li/Bi <sub>2</sub> Pb <sub>2</sub> O <sub>5</sub>	1.5	1.5	185	275	1.85	145	500
Li/MnO <sub>2</sub> <sup>‡</sup>	3.0	2.85	160	450	3.0	150	410
Li/Ag <sub>2</sub> CrO <sub>4</sub>	3.0	3/2.7	130	370	1.7	215	670

\*At approximately C/500 rate.

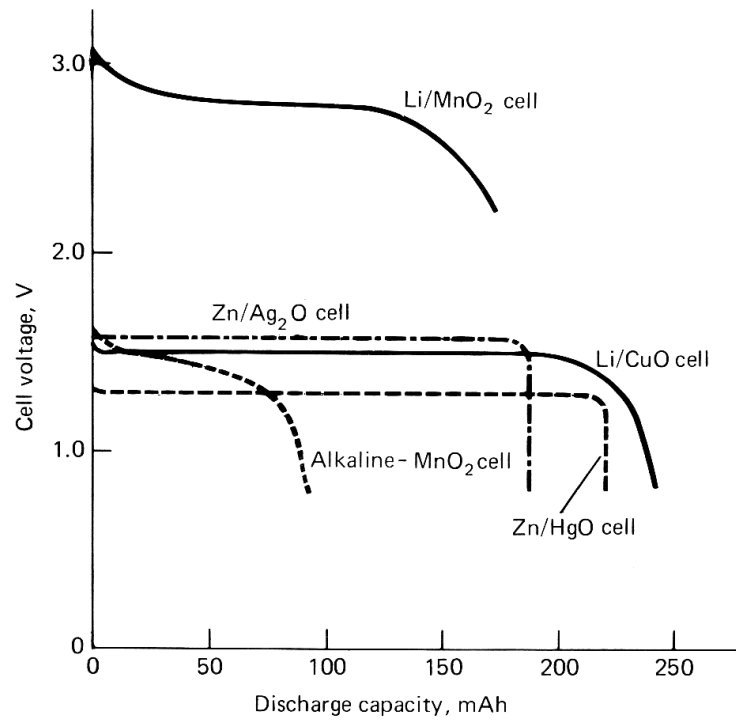
<sup>†</sup>Experimental 11.6 mm diam.  $\times$  3.6 mm high.

<sup>‡</sup> $\frac{1}{3}M$ , equivalent to two each "44" cells, 11.6 mm diam.  $\times$  10.8 mm high.

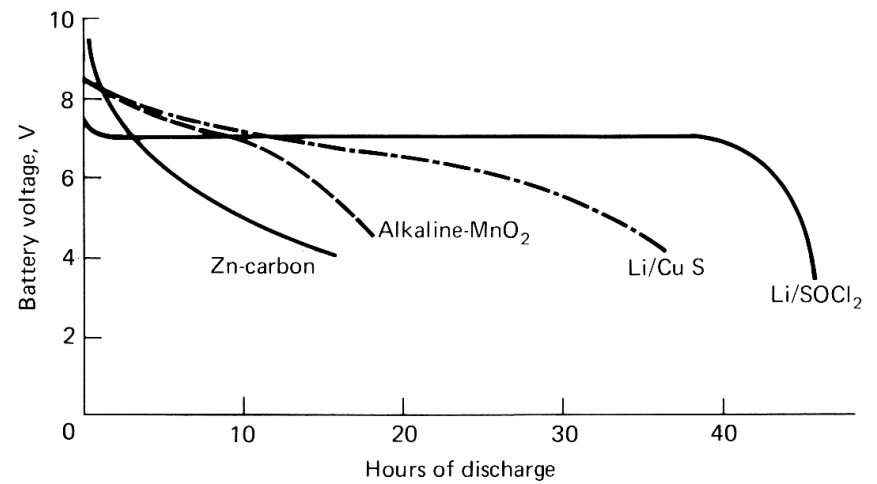
# Confronto di batterie primarie



Performance capabilities of various battery systems.

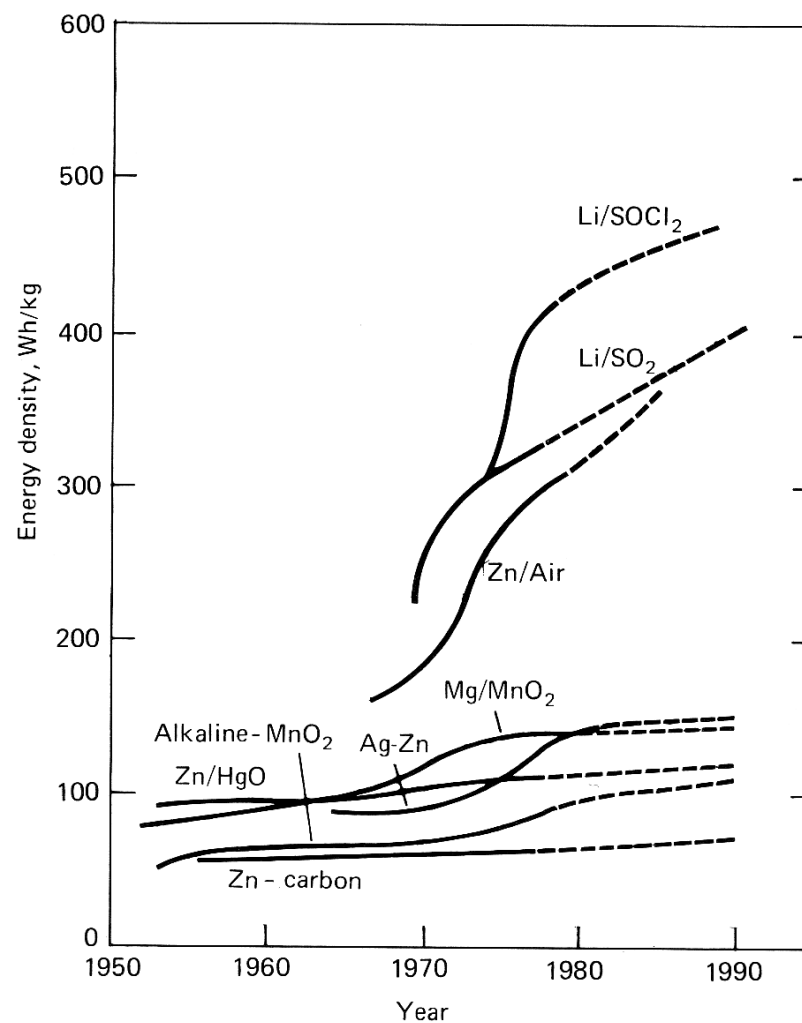


Typical discharge curves for primary battery systems, button cell: 11.6 mm diameter, 5.4 mm high.



Typical discharge curves for primary battery systems, NEDA 1604 cell, 9-V, 250 Ω discharge load.

## Miglioramenti delle prestazioni delle batterie primarie negli anni

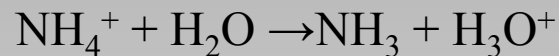
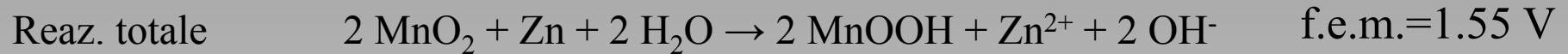
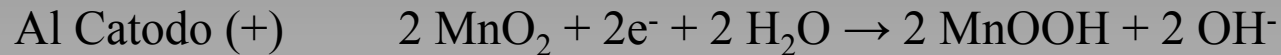


Advances in the development of primary cells, continuous discharge at 20°C, 40- to 60-h rate, D or similar size cell (solid line, historical data; broken line, forecast).

# Pile Zinco – Carbone (Leclanche)

Chimica della batteria

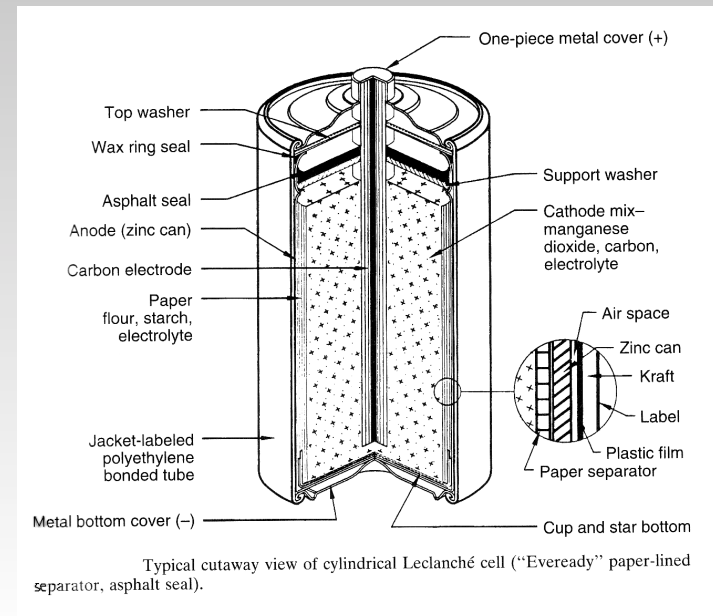
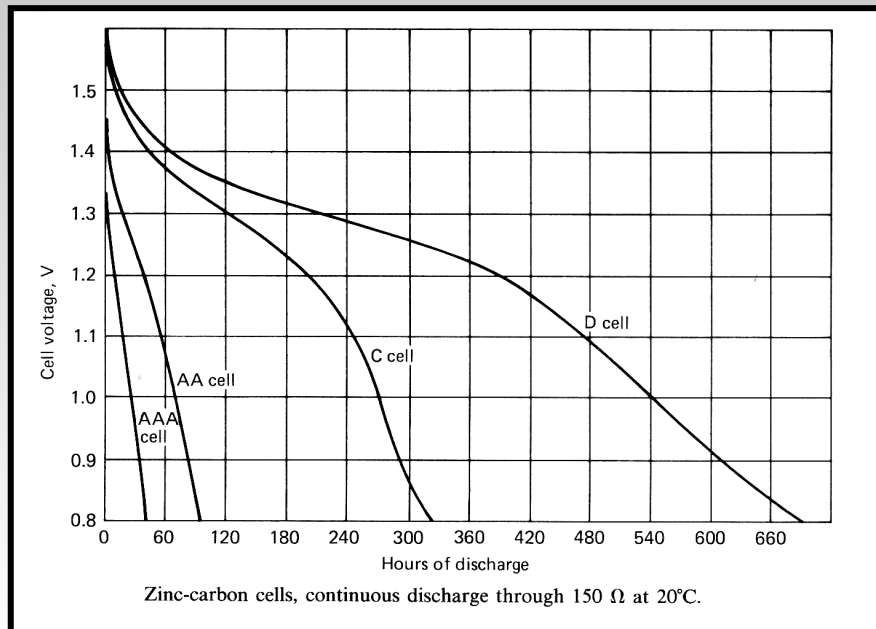
Elettrolitica: soluz. Acq. di  $\text{NH}_4\text{Cl}$



Potenziale di esercizio ~1.2 V

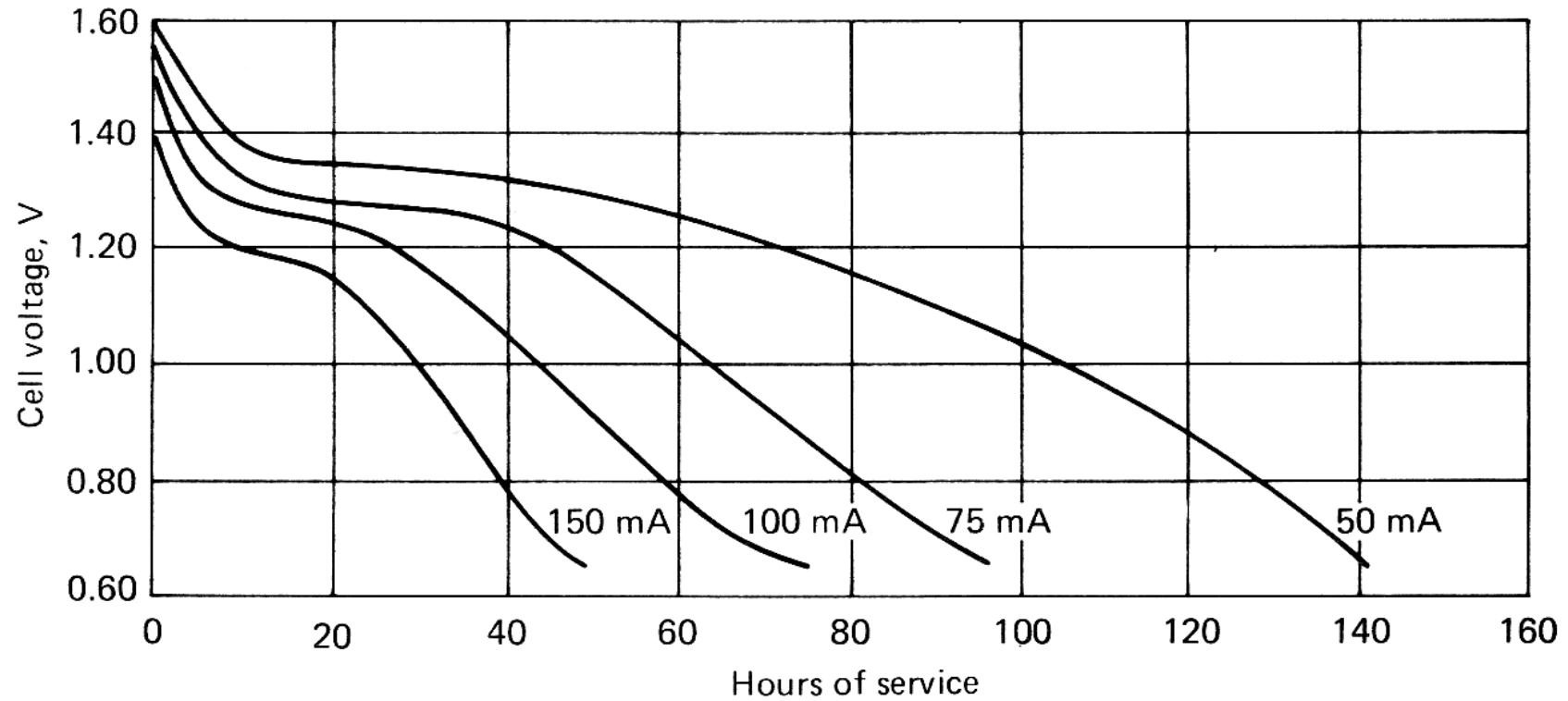
Densità di energia

85 Wh/kg 165 Wh/lit



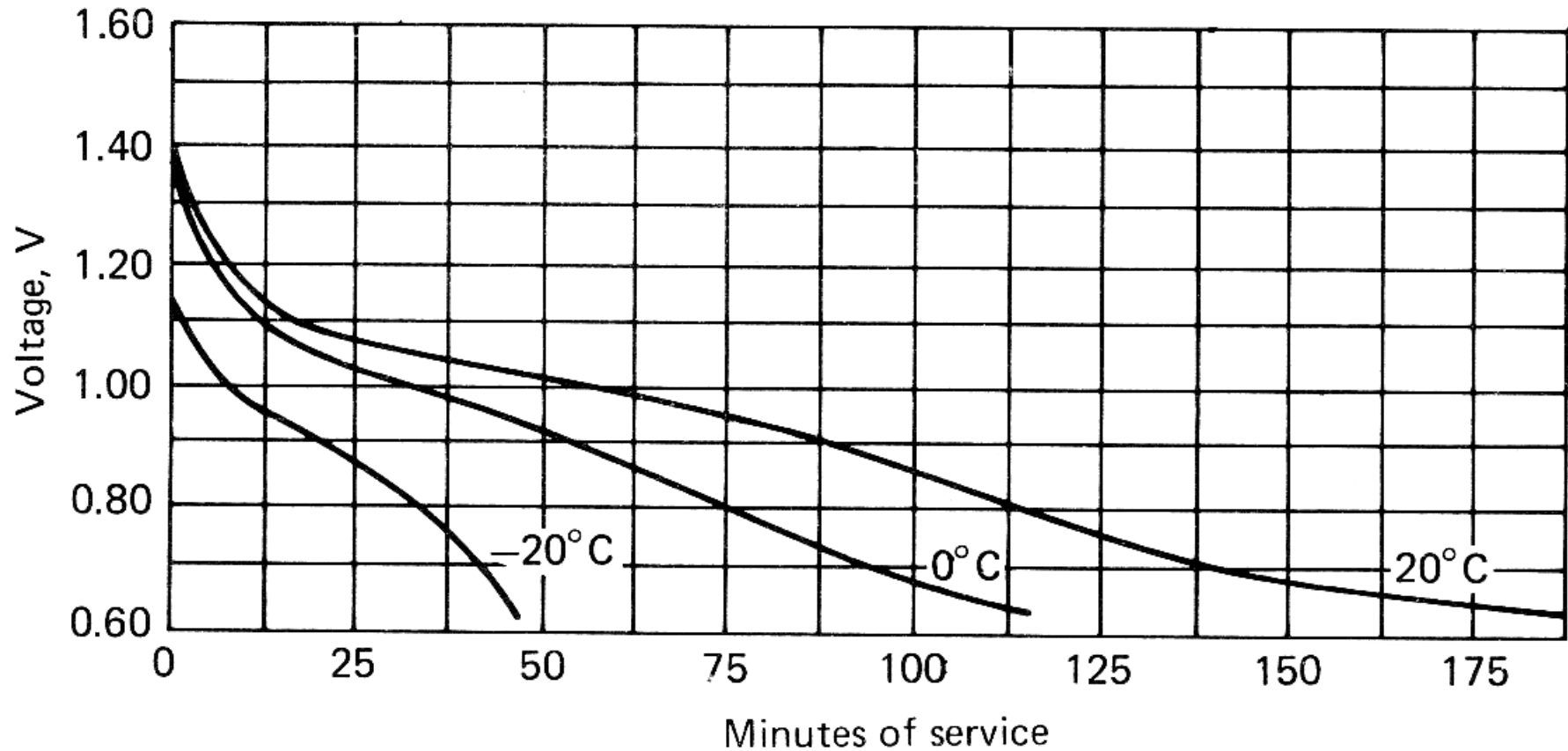


## Pile Zinco – Carbone (Leclanche)



Typical discharge curves for Leclanche zinc-carbon cell (D size), discharged 2h/day at 20°C.

## Pile Zinco – Carbone (Leclanche)



Effect of temperature on voltage characteristics of D size zinc-carbon cell, continuous discharge starting at 667 mA.

# Pile Zinco – MnO<sub>2</sub> (Leclanche alcalina)

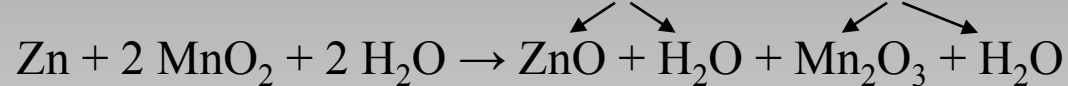
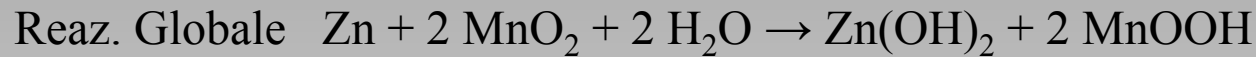
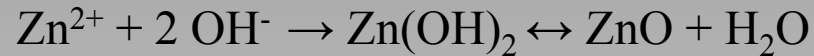
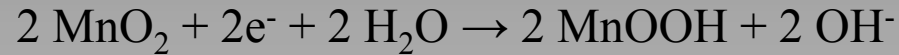
Soluzione elettrolitica di KOH

Chimica della batteria

All' anodo (-)



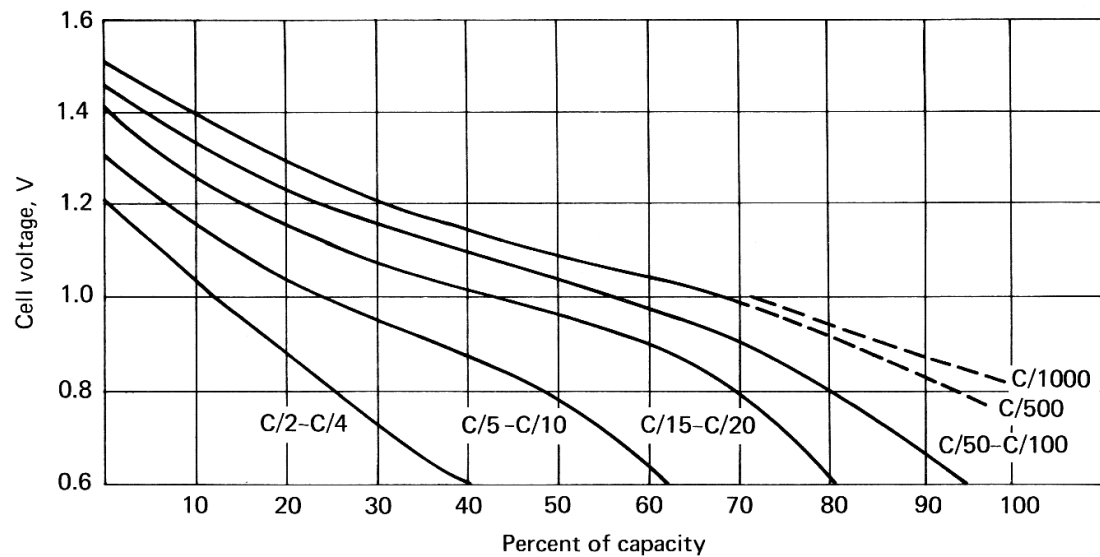
Al Catodo (+)



Densità di energia

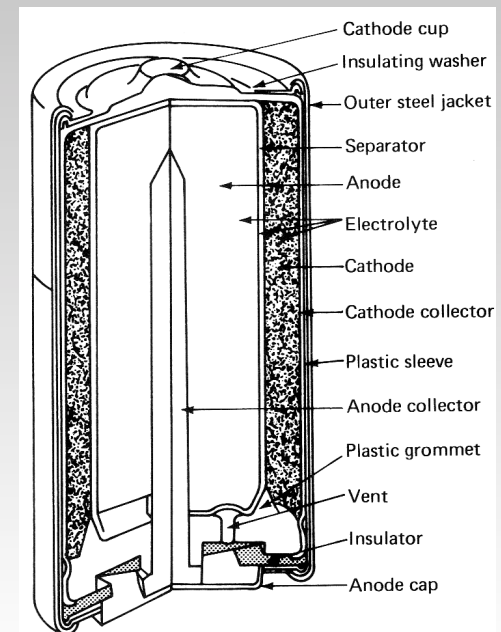
85 Wh/kg      165 Wh/lit

f.e.m.=1.55 V

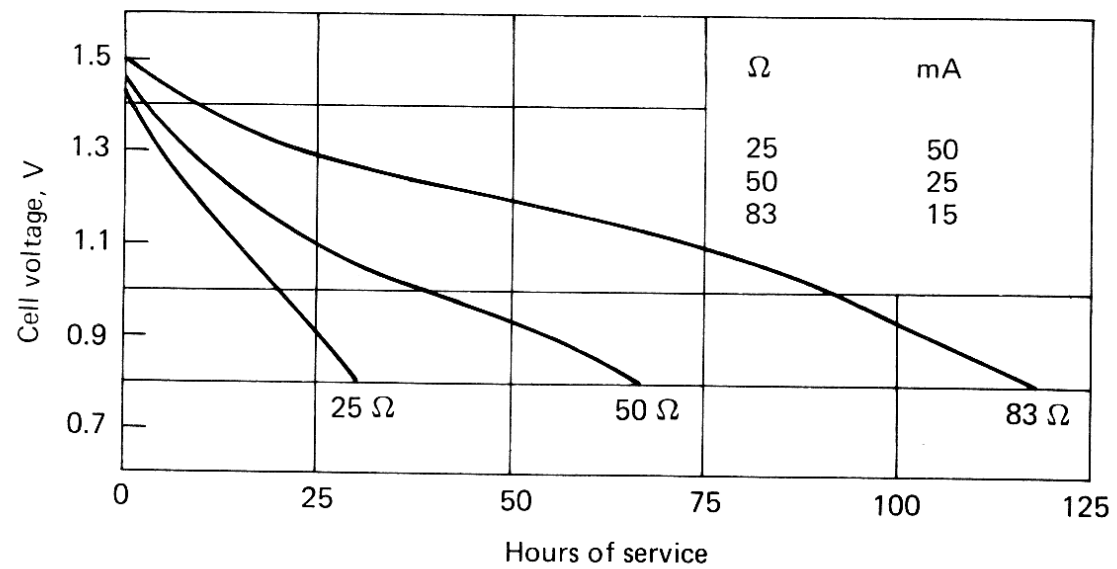
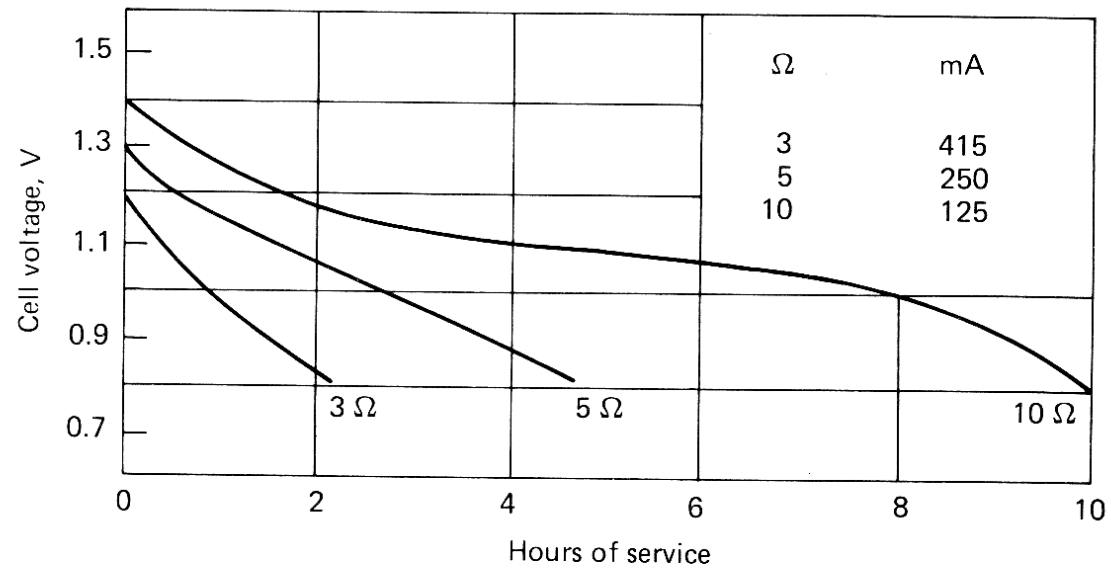


Voltage and capacity of alkaline manganese dioxide cells as a function of discharge rate at 20°C.

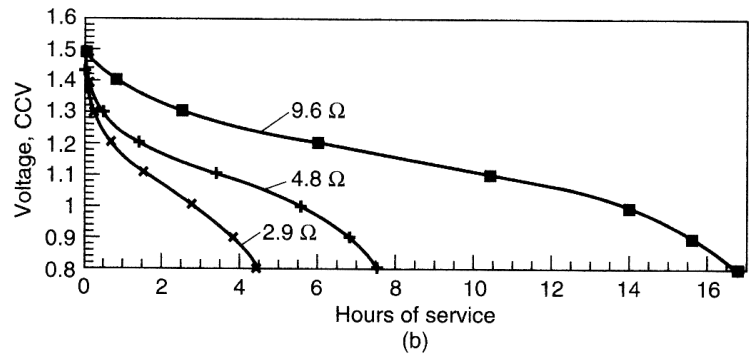
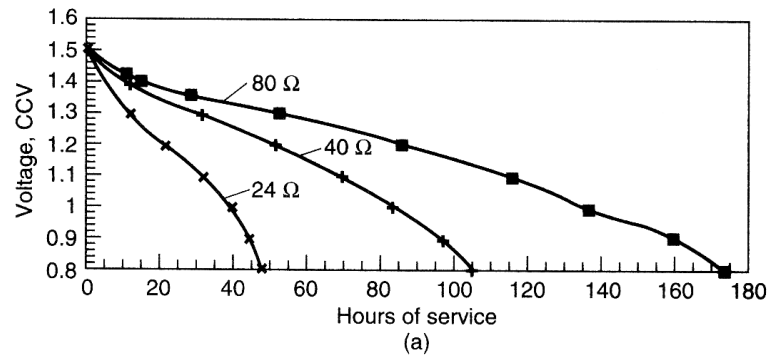
Potenziale di esercizio ~1.2 V



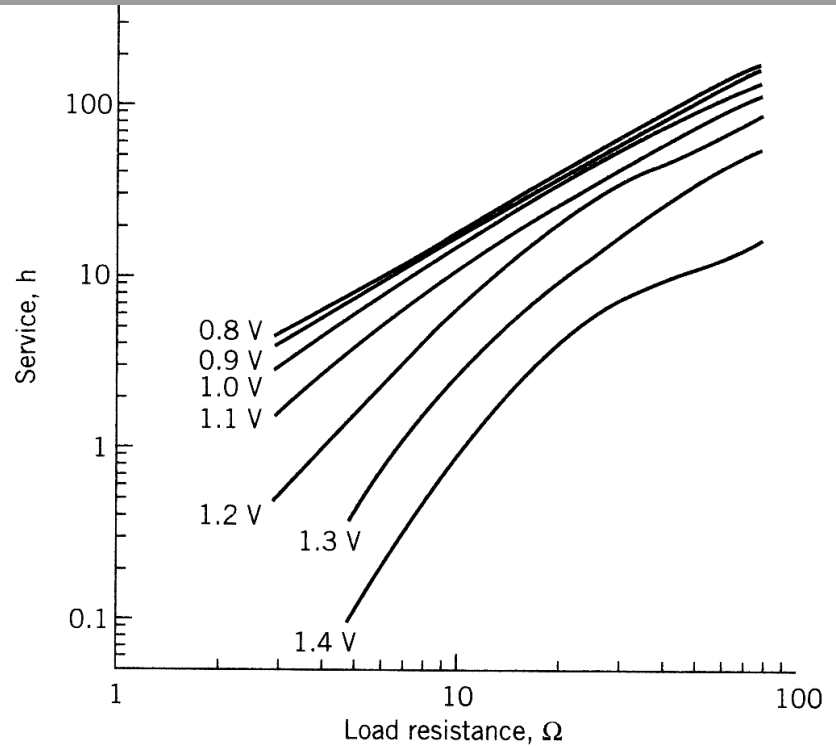
# Pile Zinco – Carbone (Leclanche alcalina)



Typical discharge curves, alkaline manganese dioxide cell (AA size) at 20°C.

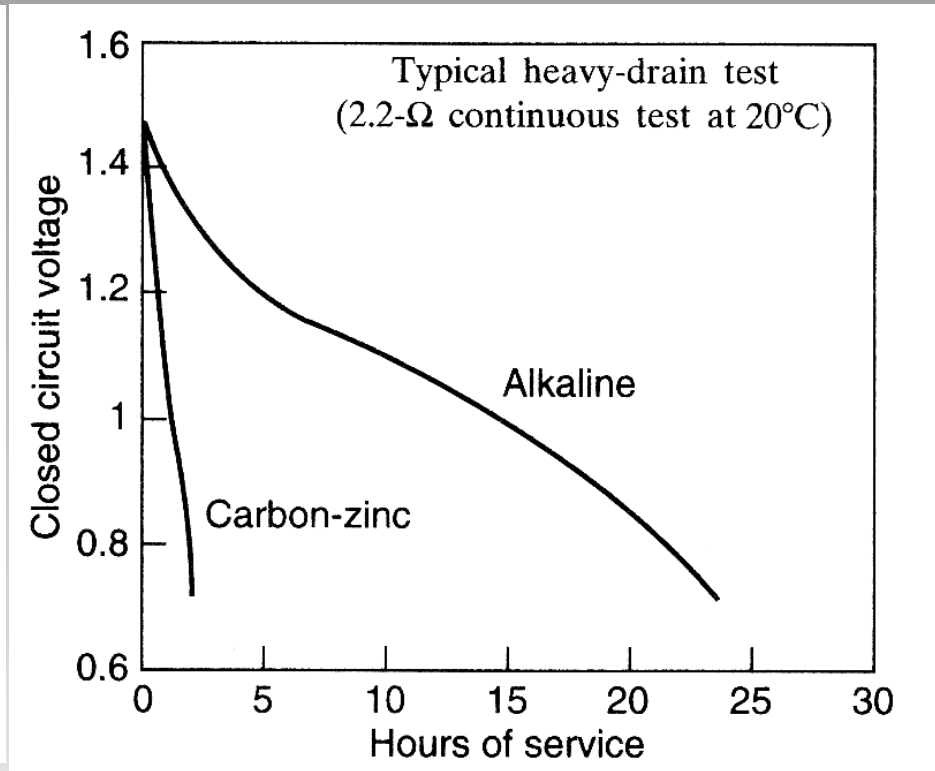
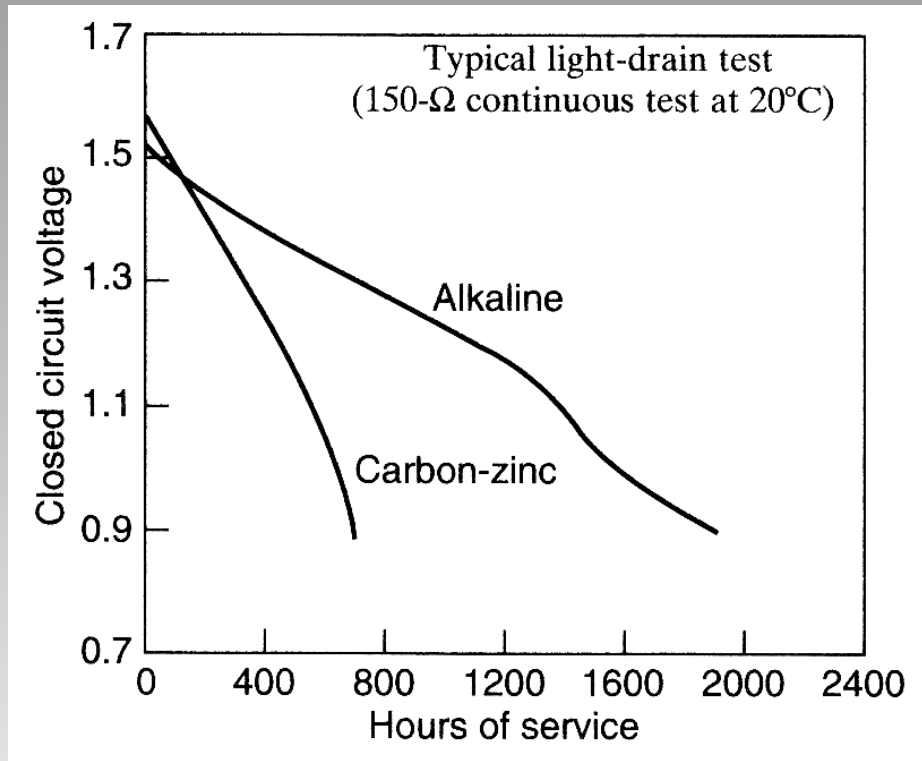


**FIGURE** Typical discharge performance characteristics for AA-size alkaline-manganese dioxide battery. (a) Continuous moderate-drain discharge at 21°C. (b) Continuous heavy-drain discharge at 21°C. (Courtesy of Eveready Battery Company.)



**FIGURE** Typical continuous discharge service to various cutoff voltages at various loads for AA-size alkaline-manganese dioxide battery at 21°C. (Courtesy of Eveready Battery Company.)

# Pile Zinco – MnO<sub>2</sub> a confronto: (Leclanche classica e alcalina)

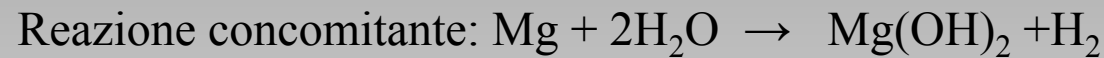
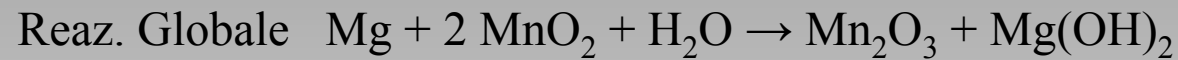
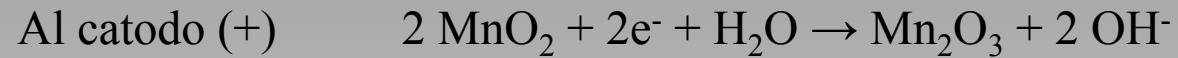
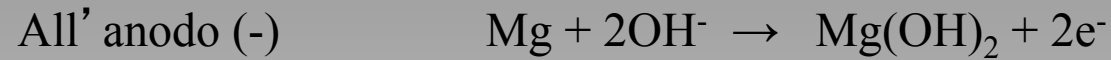


# Pile Magnesio Alluminio

Soluzione elettrolitica di KOH

f.e.m.=1.9 V

Chimica della batteria



Potenziale di esercizio ~1.7 V

Densità di energia

125 Wh/kg    330 Wh/lit

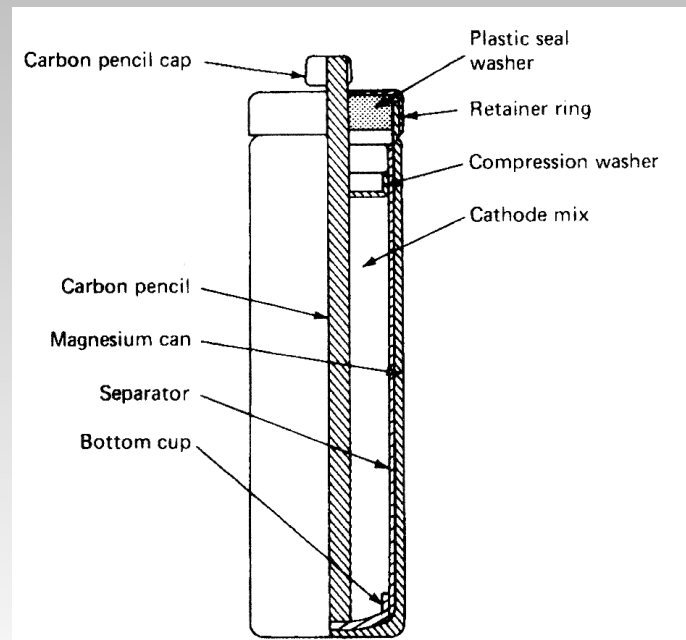
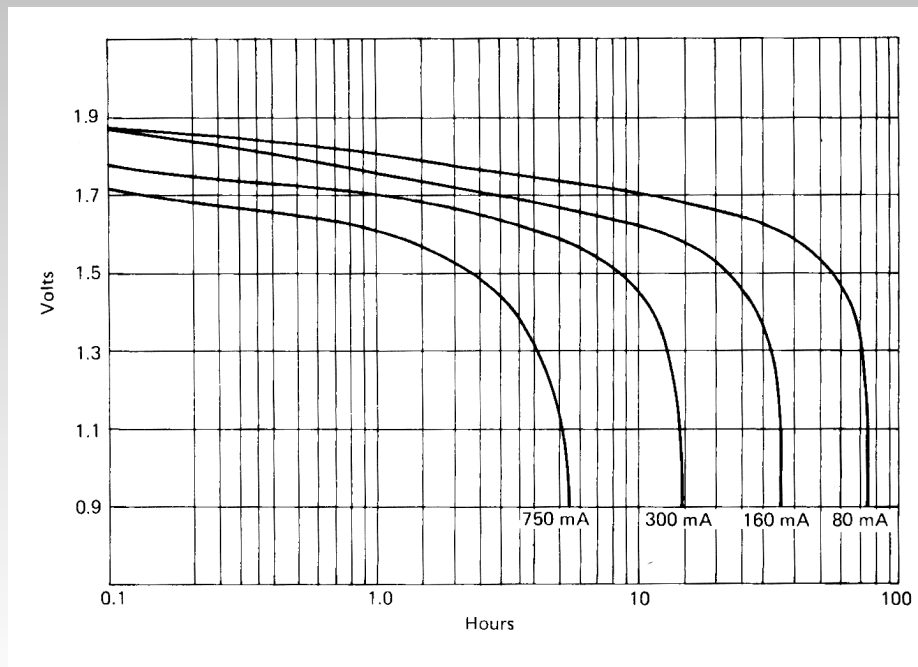


FIGURE Cylindrical construction of magnesium primary cell.

# Pile ad ossido di mercurio Ruben- Mallory

Soluzione elettrolitica di KOH

Chimica della batteria

f.e.m.=1.35 V

Al catodo (+)  $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg} + 2 \text{OH}^-$

Potenziale di esercizio~1.25 V

All' anodo (-)  $\text{Zn} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_2 + 2\text{e}^- \leftrightarrow \text{ZnO} + \text{H}_2\text{O}$

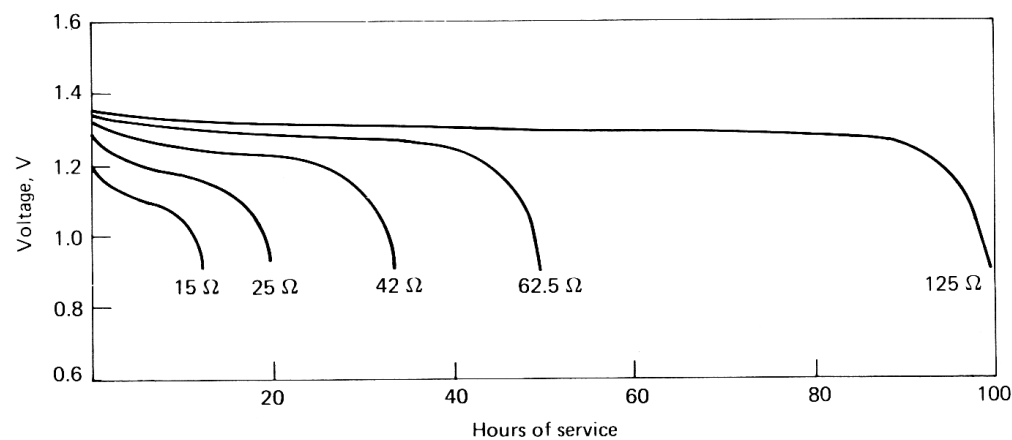
Reaz. Globale  $\text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$

Densità di energia

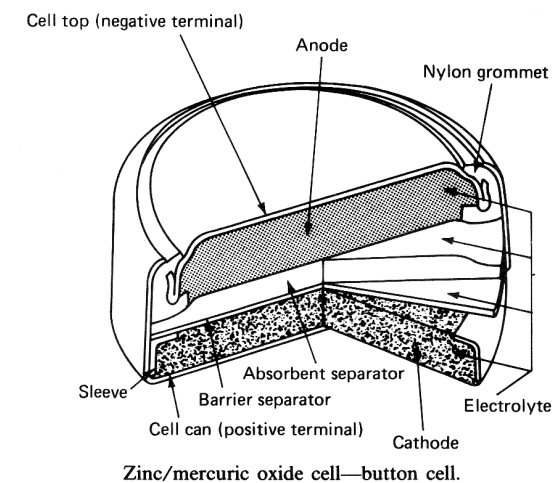
Rimane costante la composizione dell' elettrolita

100 Wh/kg 470 Wh/lit

Hg che si forma essendo un metallo mantiene elevata la conducibilità elettronica del catodo



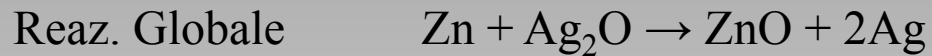
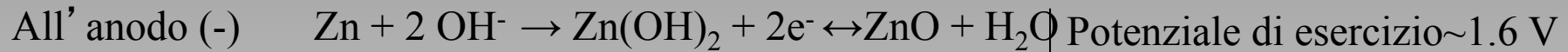
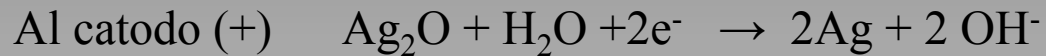
Discharge curves, R50 size zinc/mercuric oxide cell, 20°C.





# Pile ad ossido di argento

## Chimica della batteria



Rimane costante la composizione dell' elettrolita

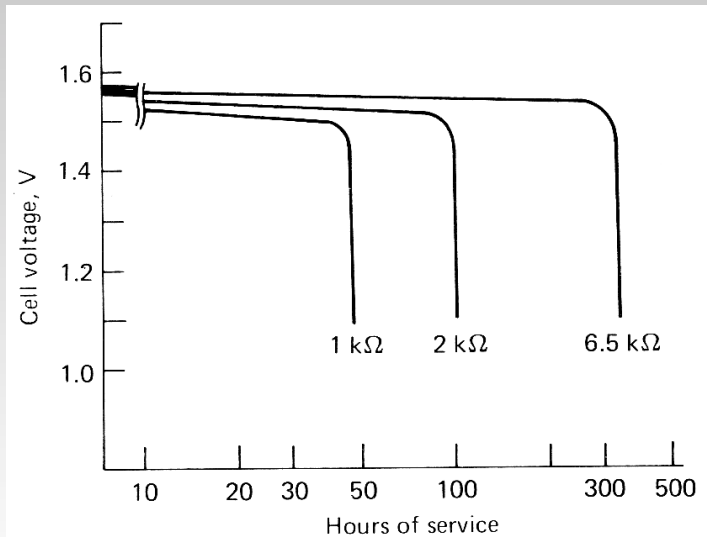
Ag che si forma essendo un metallo mantiene elevata la conducibilità elettronica del catodo

## Soluzione elettrolitica di KOH

f.e.m.=1.8 V

Densità di energia

120 Wh/kg    500 Wh/lit



Typical discharge curves of zinc/silver oxide cell at 20°C (size: 11.6 × 3.0 mm).

