

## **PILE A LITIO A CATODO SOLIDO: $\text{Li/MnO}_2$**

Studiata e realizzata nei primi anni '70,  $\text{Li-MnO}_2$  è stata la prima pila al litio ad essere commercializzata per moltissime applicazioni ed ancora oggi è ancora la pila primaria più utilizzata.

**alto voltaggio (3 V)**

**alta densità di energia: 200-250 Wh/kg,**

(2-4 volte le pile alcaline)

**buona stabilità,**

(migliore di alluminio e magnesio)

**ampio range di temperatura (-20°C - +60°C)**

**curva di scarica piatta**

**elevato tempo di storage**

(5-8 anni)

**assemblaggio molto semplice**

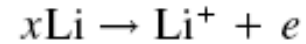
basta un contenitore di plastica serrato meccanicamente

**basso costo**

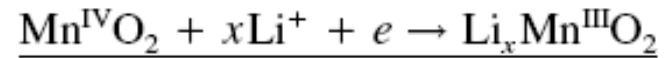
$\text{MnO}_2$  è ottenuto per precipitazione da soluzioni acquose in dimensioni micrometriche che viene comunque macinato

# Reazione d'intercalazione

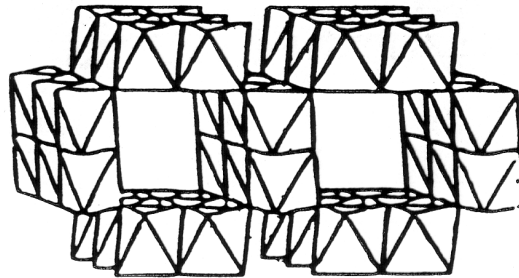
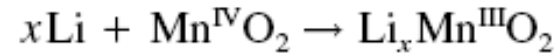
Anode



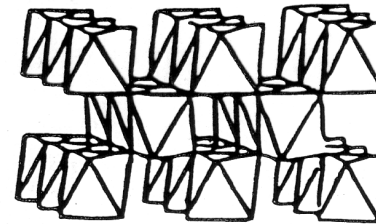
Cathode



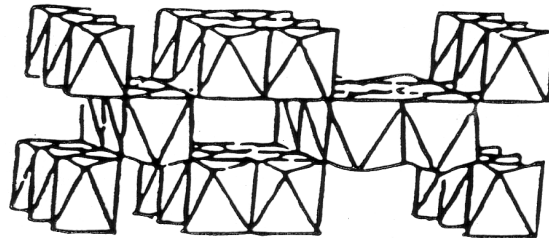
Overall



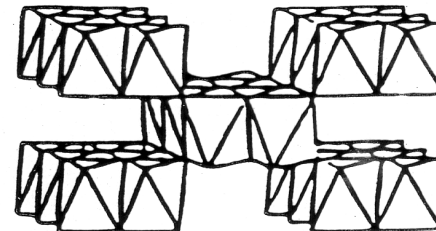
$\alpha$ -MnO<sub>2</sub>



$\beta$ -MnO<sub>2</sub>



$\gamma$ -MnO<sub>2</sub>



Ramsdellite

Fig. 1. MnO<sub>2</sub> polymorphs showing the different tunnel shapes.

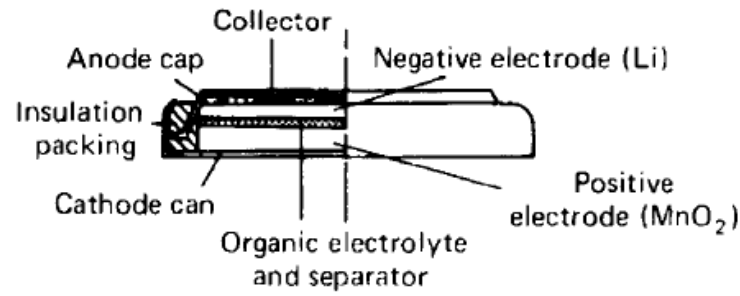


FIGURE Cross-sectional view of Li/MnO<sub>2</sub> coin-type battery.

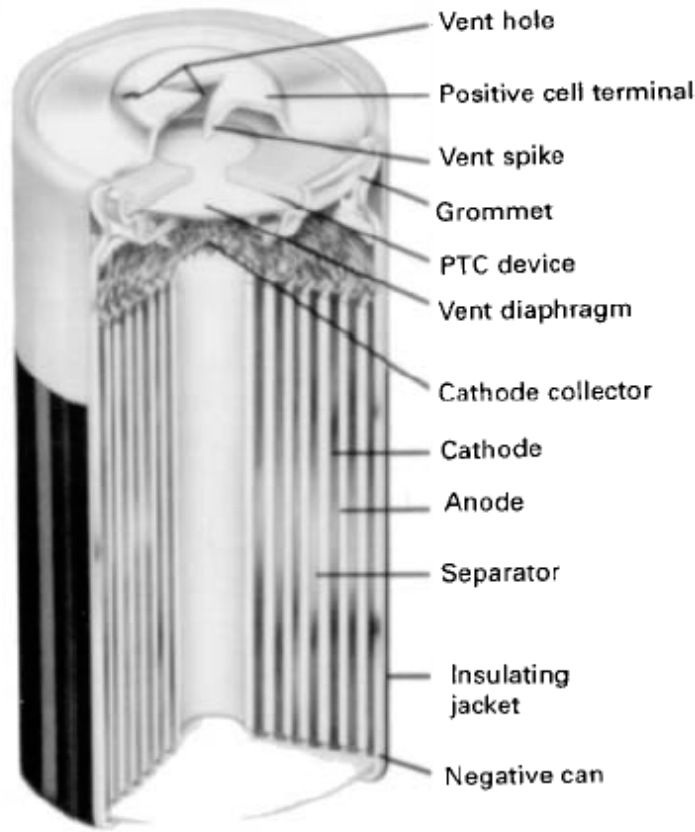


FIGURE Cross-sectional view of Li/MnO<sub>2</sub> spirally wound electrode battery.

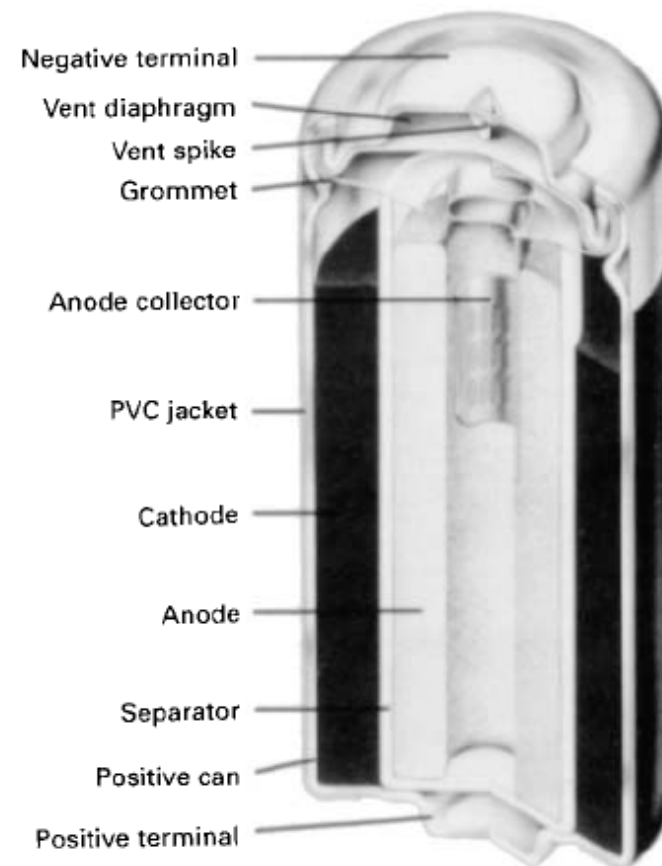
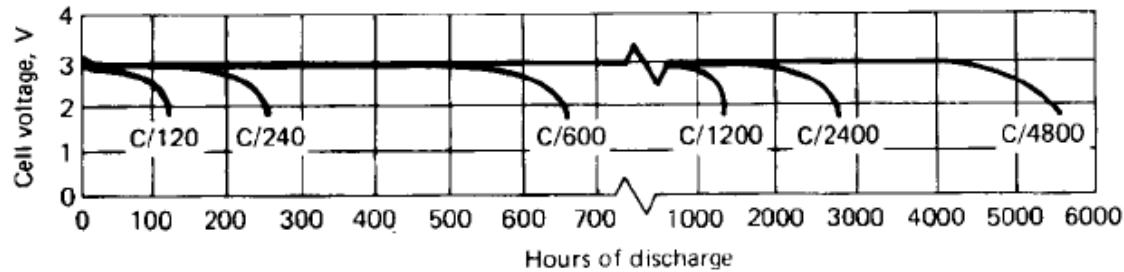


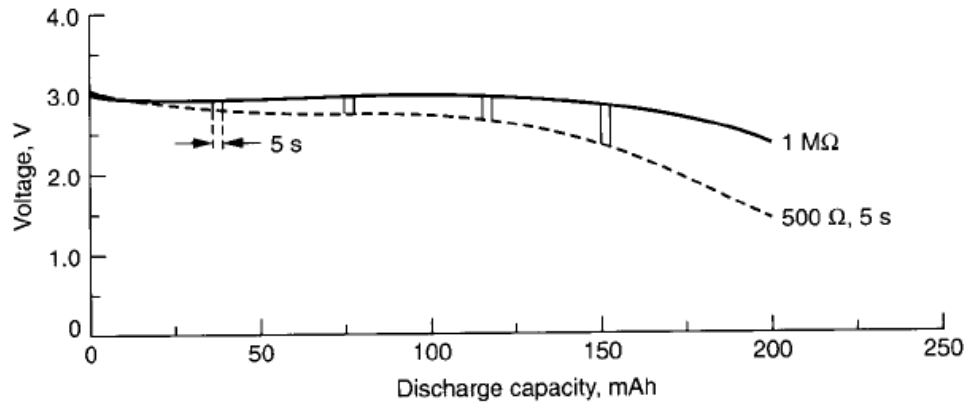
FIGURE Cross-sectional view of Li/MnO<sub>2</sub> bobbin battery.

# Coin cells



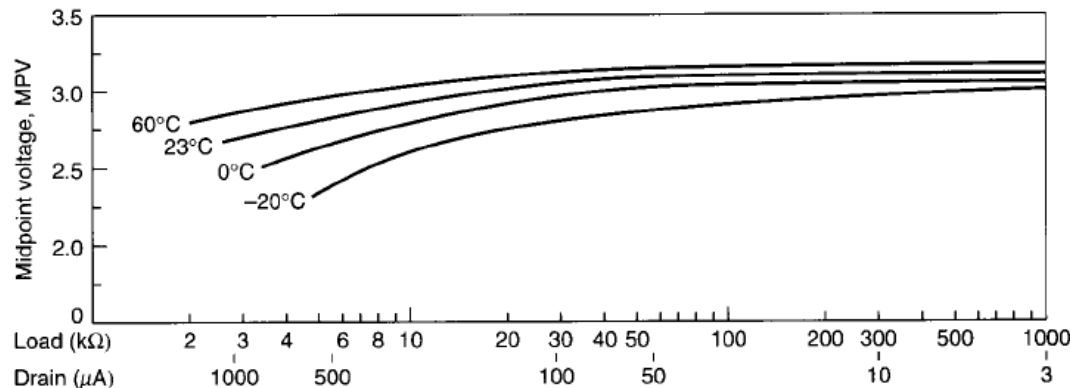
Potenziale molto piatto

FIGURE Typical discharge curves of Li/MnO<sub>2</sub> coin-type batteries.



Regge bene gli impulsi di corrente

FIGURE Pulse characteristics of Li/MnO<sub>2</sub> coin-type battery (190-mAh size) at 20°C. Test conditions: continuous load 1 MΩ ≈ 3 μA; pulse load 500 Ω ≈ 5.5 mA; duration 5 s; pulses 4; time between pulses 3 h.



L'effetto della temperatura si fa sentire solo quando aumenta la corrente

FIGURE Midpoint voltage during discharge of Li/MnO<sub>2</sub> coin-type (280-mAh size).

# Cylindrical Bobbin Batteries.

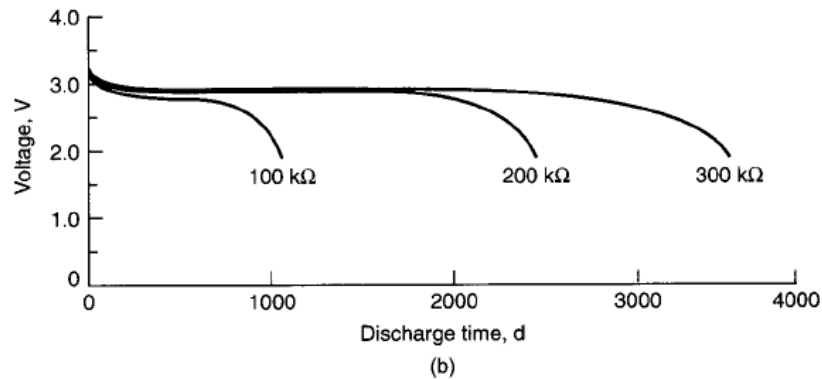
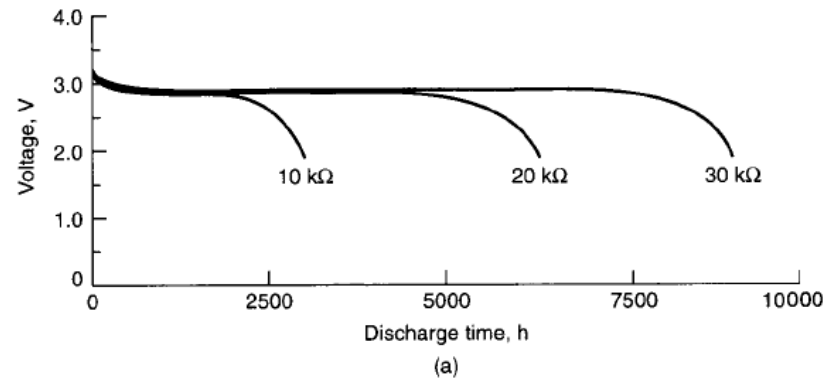
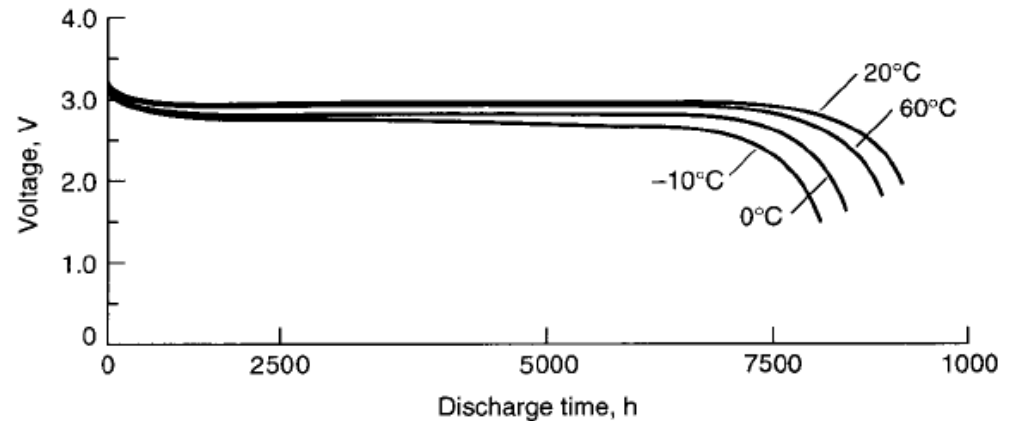
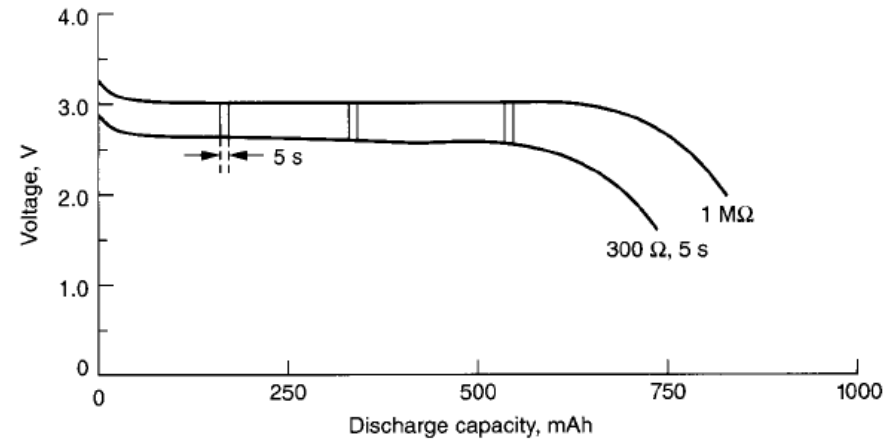
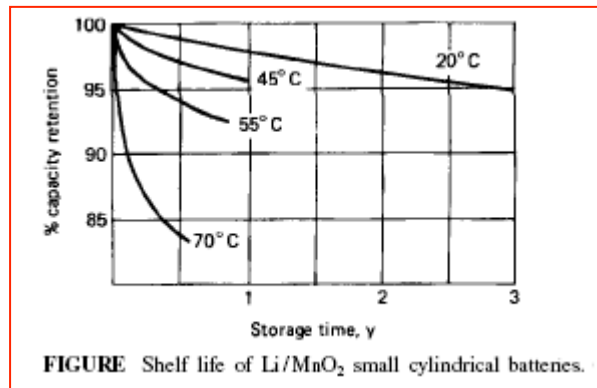


FIGURE Discharge characteristics of Li/MnO<sub>2</sub> cylindrical bobbin battery (850-mAh size) at 20°C. (a) Discharge time in hours. (b) Discharge time in days.



**TABLE** Typical Li/MnO<sub>2</sub> Batteries

International (IEC) type	Rated capacity, mAh*	Weight, g	Diameter, mm	Height, mm	Volume, cm <sup>3</sup>	Specific energy Wh/kg	Energy† density Wh/L	Impedance at 1 kHz, Ω
Low-rate flat or coin batteries, 3 V								
CR 1216	25	0.7	12.5	1.6	0.21	100	335	—
CR 1025	30	0.7	10.0	2.5	0.20	125	410	—
CR 1220	35	0.9	12.5	2.0	0.25	110	390	—
CR 1616	55	1.2	16.0	1.6	0.32	128	480	—
CR 2012	55	1.4	20.0	1.2	0.38	110	405	—
CR 1620	70	1.3	16.0	2.0	0.40	150	485	—
CR 2016	75	1.7	20.0	1.6	0.50	125	420	12–18
CR 2320	130	3.0	23.0	2.0	0.83	122	440	—
CR 2025	150	2.5	20.0	2.5	0.79	165	530	12–18
CR 2325	190	3.0	23.0	2.5	1.04	175	510	8–15
CR 2032	210	3.3	20.0	3.2	1.00	175	585	12–18
CR 2330	265	4.0	23.0	3.0	1.35	185	550	—
CR 2430	280	4.0	24.5	3.0	1.41	195	555	8–15
CR 3032	500	7.1	30.0	3.2	2.26	195	600	—
CR 2450	550	6.2	24.5	5.0	2.35	245	650	8–15
CR 2354	560	5.9	23.0	5.4	2.24	205	700	—
CR 2477	1000	10.5	24.5	7.7	3.62	260	770	—
Cylindrical batteries; spirally wound, 3 V								
CR 11108‡	160	3.3	11.6	10.8	1.14	155	395	3–5
CR 15H270‡	750	11.0	15.6	27.0	5.2	190	400	—
CR 17345‡	1400	17.0	17.	34.5	7.8	230	535	2–6
Cylindrical batteries, bobbin, 3 V								
CR 14250	850	9.5	14.5	25.0	11.1	250	580	9–13
CR 17335	1800	17.	17.	33.5	7.6	295	660	5–8
Batteries (dimensions in mm)								
2 CR $\frac{1}{3}$ N	160	9.4	13.0 (D) × 25.2 (H)			2 CR $\frac{1}{3}$ N cells in series, 6 V		
2 CR 5	1300	37.	17 (T) × 34 (W) × 45 (H)			2 CR 17345 cells in series, 6 V		
CR-P2	1300	37.	19.5 (T) × 34 (W) × 36 (H)			2 CR 17345 cells in series, 6 V		
1604LE	1200	34.4	16.8 (T) × 25.8 (W) × 48.4 (H)			3 prismatic cells in series, 9 V		
CR-V6	1500	39.	29 (W) × 14.5 (T) × 52 (H)			2 "AA"-size cells in series, 6 V		
CR-V3	3000	34.	29 (W) × 14.5 (T) × 52 (H)			2 "AA"-size cells in parallel, 3 V		

\* Low-rate batteries—C/200 rate; high-rate and cylindrical cells—C/30 rate.

† Based on average voltage of 2.8 V.

‡ Common nomenclature: CR 11108 — CR  $\frac{1}{3}$ N; CR 15H270 — CR 2; CR 17345 — CR 123A.

Source: Manufacturers' data sheets.

# Sicurezza

## Fattori di rischio:

- La temperatura di fusione del litio è di circa 180°C
- Le soluzioni elettrolitiche organiche sono infiammabili
- Una pila potrebbe essere dismessa quando non è ancora completamente scarica  
**la rottura accidentale dell'involucro potrebbe causare un'esplosione.**

## Dispositivi di sicurezza previsti nelle pile:

### Sistemi irreversibili

- Le celle sono previste di valvole di sicurezza per evitare sovrappressione interna
- Elementi fusibili che si interrompono in presenza di un cortocircuito interno

### Sistemi reversibili

per pile di grandi capacità si usa un dispositivo chiamato PTC (positive temperature coefficient): elemento interno che aumenta esponenzialmente la sua resistenza elettrica in caso di elevate temperature, facendo tornare i livelli di scarica nei margini di sicurezza (aumenta la resistenza interna della pila), e quanto la T diminuisce, la pila torna a funzionare normalmente