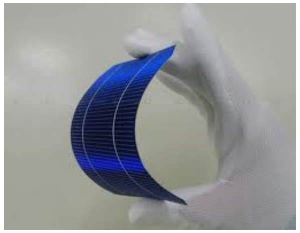
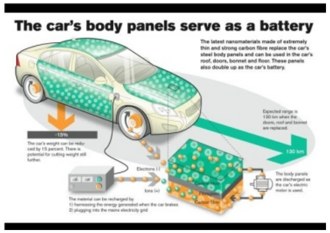
Materiali per l’Energetica

Prof. Vito Di Noto





Nomenclatura

- Cella o batteria: sorgente di potenza elettrochimico chiuso (i reagenti sono stati incorporati durante la costruzione).

Il termine batteria indica una cella singola o un gruppo di celle

- Cella primaria: sistema la cui vita termina una volta che i reagenti sono stati consumati
- Cella secondaria: sistema che può essere ricaricato o caricato quando i suoi reagenti sono stati consumati
- Cella a combustibile: sorgente di potenza elettrochimica aperta (Sistema in cui i reagenti catodici ed anodici sono stati immagazzinati esternamente e possono essere forniti alla cella elettrochimica in modo continuo)
- Cella ibrido: sorgente di potenza in cui uno dei reagenti attivi è fornito allo stato gassoso – per esempio O_2 dell’aria

Convenzione di scrittura

Sinistro	Destro
Elettrodo negativo	Elettrodo positivo
(**a**nodo)	(**c**atodo)

TRE ECCEZIONI

Nomenclatura convenzionale	**Nome comune**
Piombo – Piombo biossido	Piombo-acido
Cadmio – Ossido di Nichel	Nichel–Cadmio
Zinco – Biossido di Manganese	Leclanchè

Es:

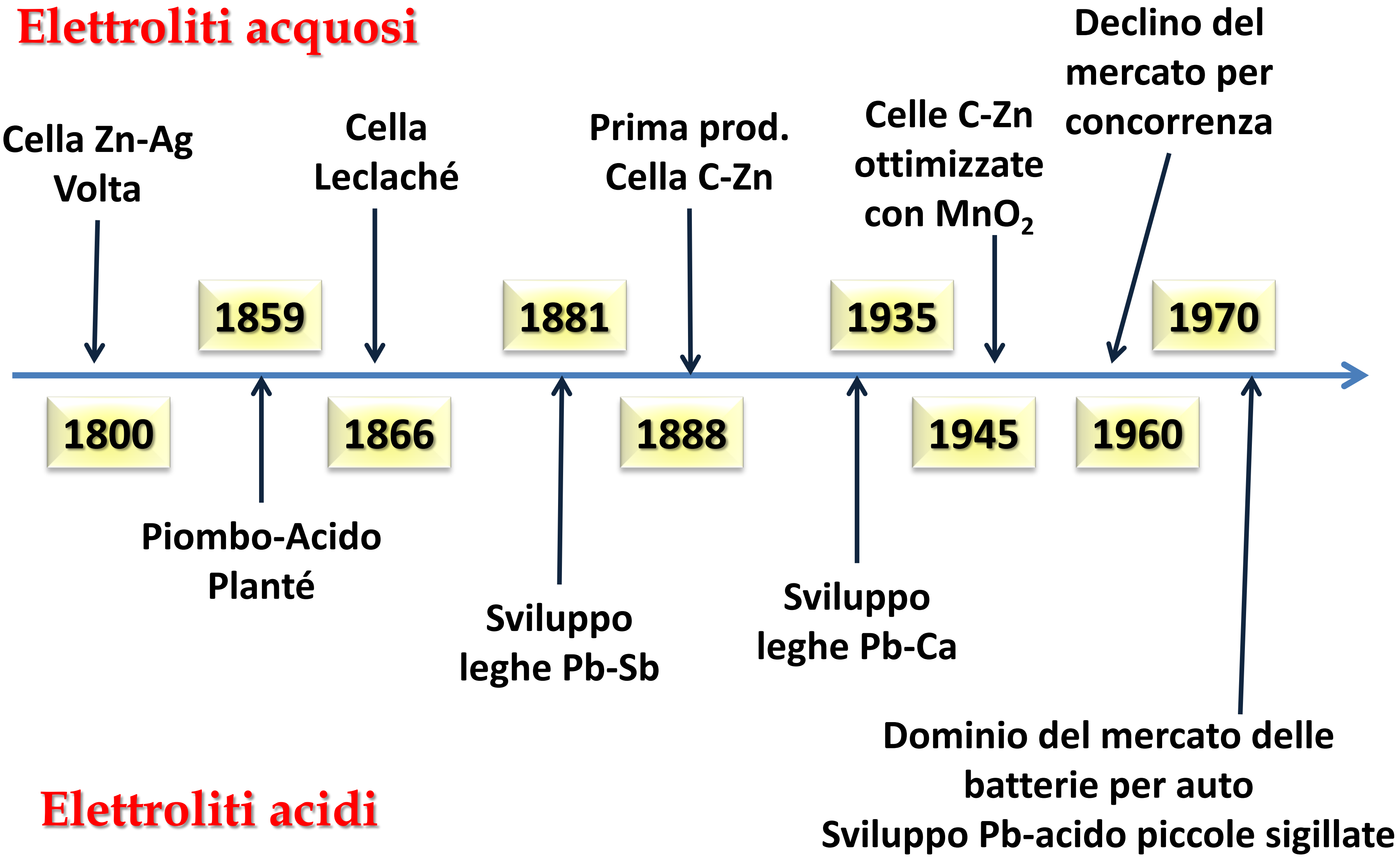
Pt, H_2(P) | HCl (m) | AgCl, Ag

| = confine tra due fasi

Pt, H_2(P) | HCl (m_L) || HCl (m_R)|H_2 (P), Pt

|| = ponte salino per eliminare la giunzione liquida

Evoluzione delle batterie acquose



Elettroliti acquosi

Cella Zn-Ag
Volta

1859

Cella
Leclaché

1881

Prima prod.
Cella C-Zn

1935

Celle C-Zn
ottimizzate
con MnO_2

Declino del
mercato per
concorrenza

1970

1800

1866

1888

1945

1960

Piombo-Acido
Planté

Sviluppo
leghe Pb-Sb

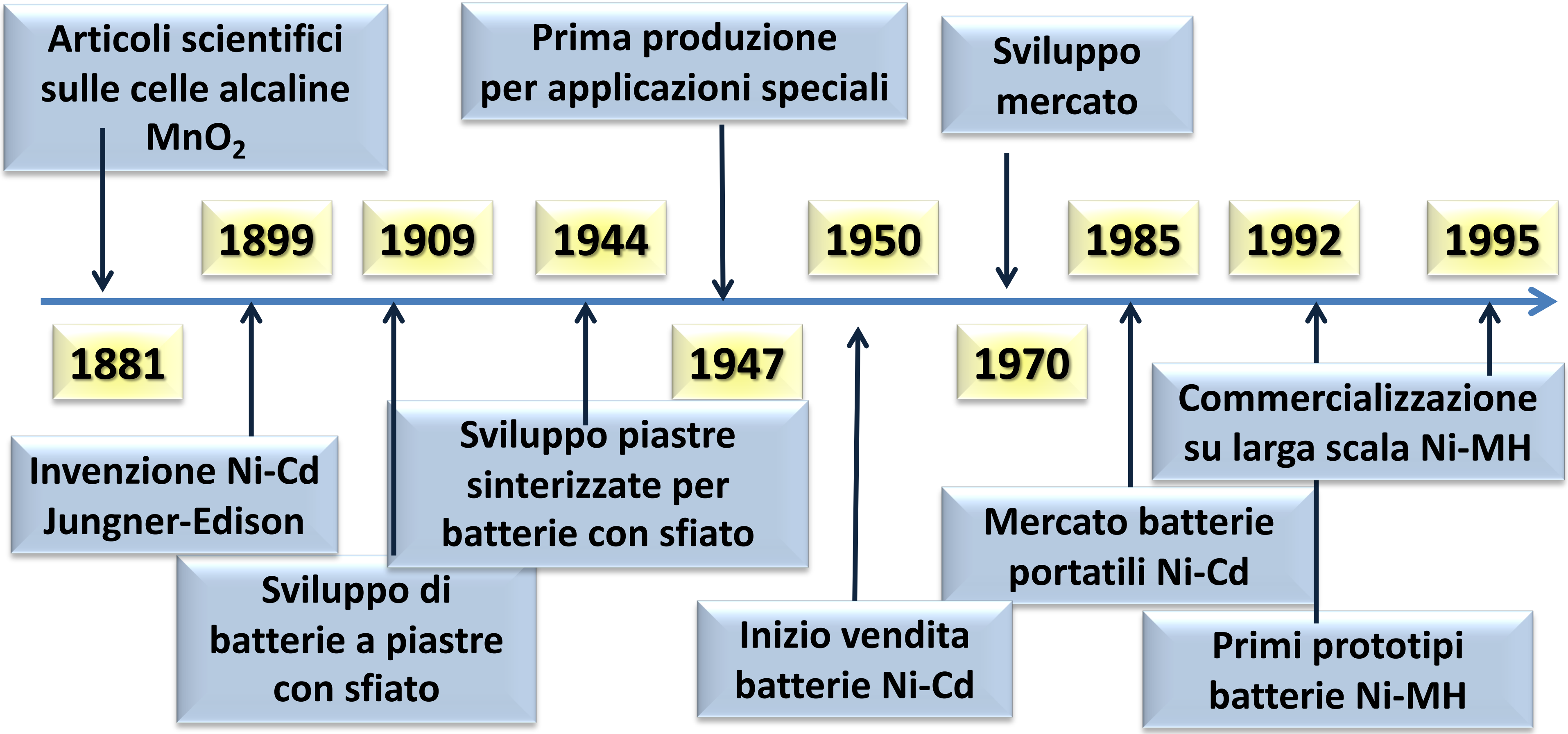
Sviluppo
leghe Pb-Ca

Dominio del mercato delle
batterie per auto
Sviluppo Pb-acido piccole sigillate

Elettroliti acidi

Evoluzione delle batterie acquose con elettrolita alcalino

Batterie primarie (non ricaricbili) MnO_2-Zn



Articoli scientifici sulle celle alcaline MnO_2

Prima produzione per applicazioni speciali

Sviluppo mercato

1899

1909

1944

1950

1985

1992

1995

1881

1947

1970

Commercializzazione su larga scala Ni-MH

Invenzione Ni-Cd Jungner-Edison

Sviluppo piastre sinterizzate per batterie con sfiato

Mercato batterie portatili Ni-Cd

Sviluppo di batterie a piastre con sfiato

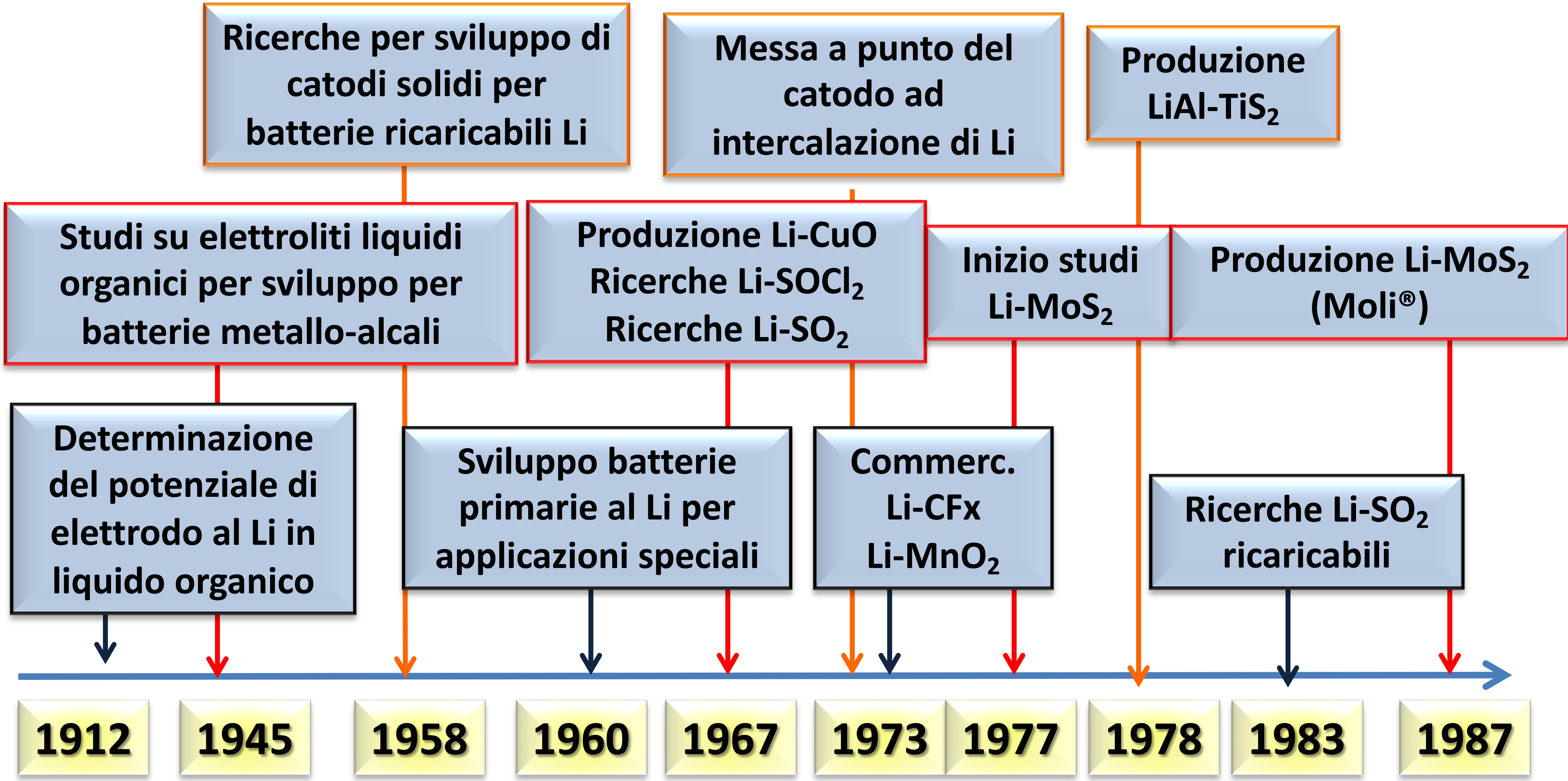
Inizio vendita batterie Ni-Cd

Primi prototipi batterie Ni-MH

Batterie secondarie (ricaricabili) Ni-Cd

Evoluzione delle batterie Alcali-Metalli

Elettrolita liquido



Ricerche per sviluppo di catodi solidi per batterie ricaricabili Li

Messa a punto del catodo ad intercalazione di Li

Produzione LiAl-TiS_2

Studi su elettroliti liquidi organici per sviluppo per batterie metallo-alcali

Produzione Li-CuO
Ricerche Li-$SOCl_2$
Ricerche Li-SO_2

Inizio studi Li-MoS_2

Produzione Li-MoS_2 (Moli®)

Determinazione del potenziale di elettrodo al Li in liquido organico

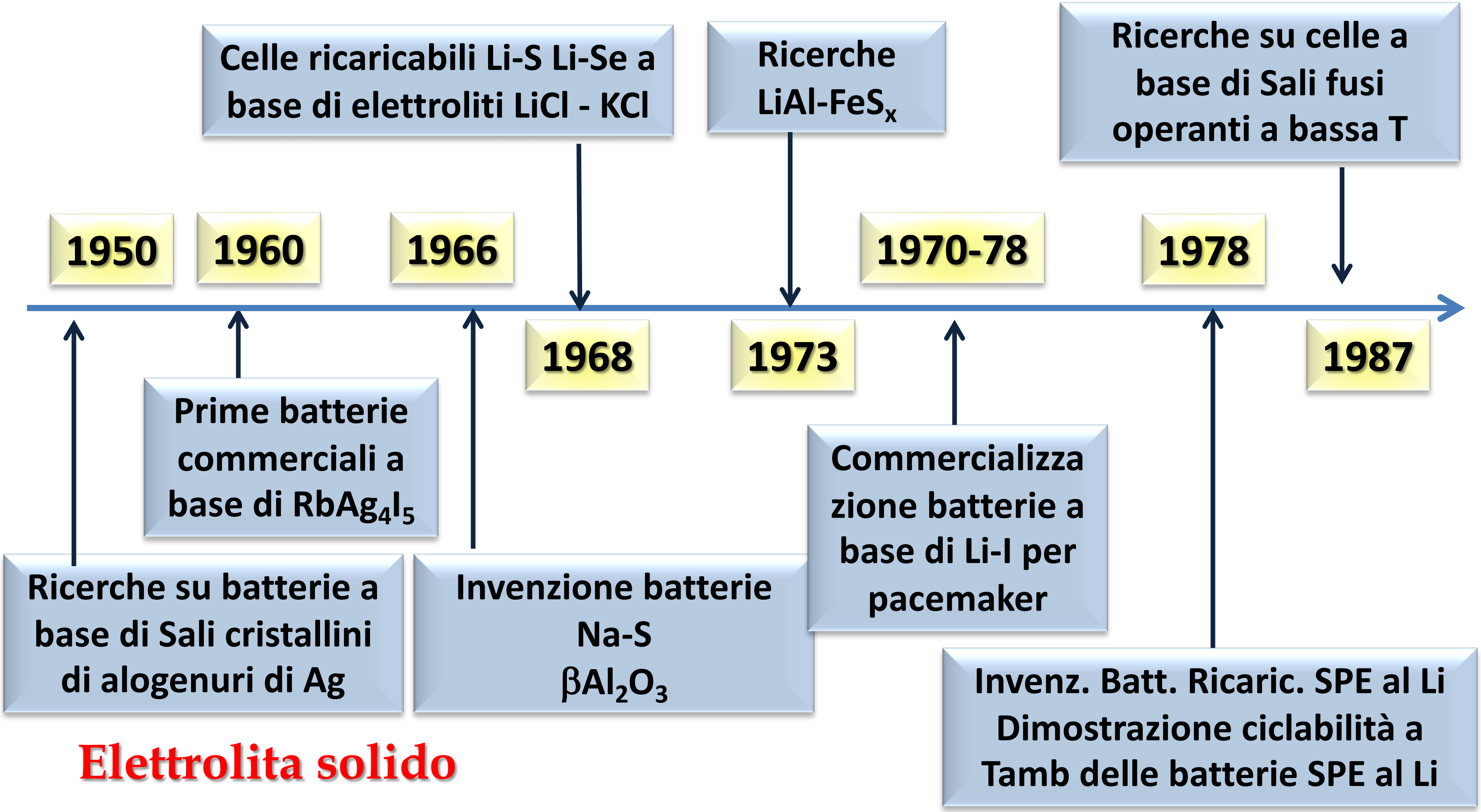
Sviluppo batterie primarie al Li per applicazioni speciali

Commerc.
Li-CFx
Li-MnO_2

Ricerche Li-SO_2 ricaricabili

1912 1945 1958 1960 1967 1973 1977 1978 1983 1987

Evoluzione delle batterie Alcali-Metalli



Elettrolita a sali fusi

Celle ricaricabili Li-S Li-Se a base di elettroliti LiCl - KCl

Ricerche $LiAl-FeS_x$

Ricerche su celle a base di Sali fusi operanti a bassa T

1950

1960

1966

1968

1973

1970-78

1978

1987

Prime batterie commerciali a base di $RbAg_4I_5$

Ricerche su batterie a base di Sali cristallini di alogenuri di Ag

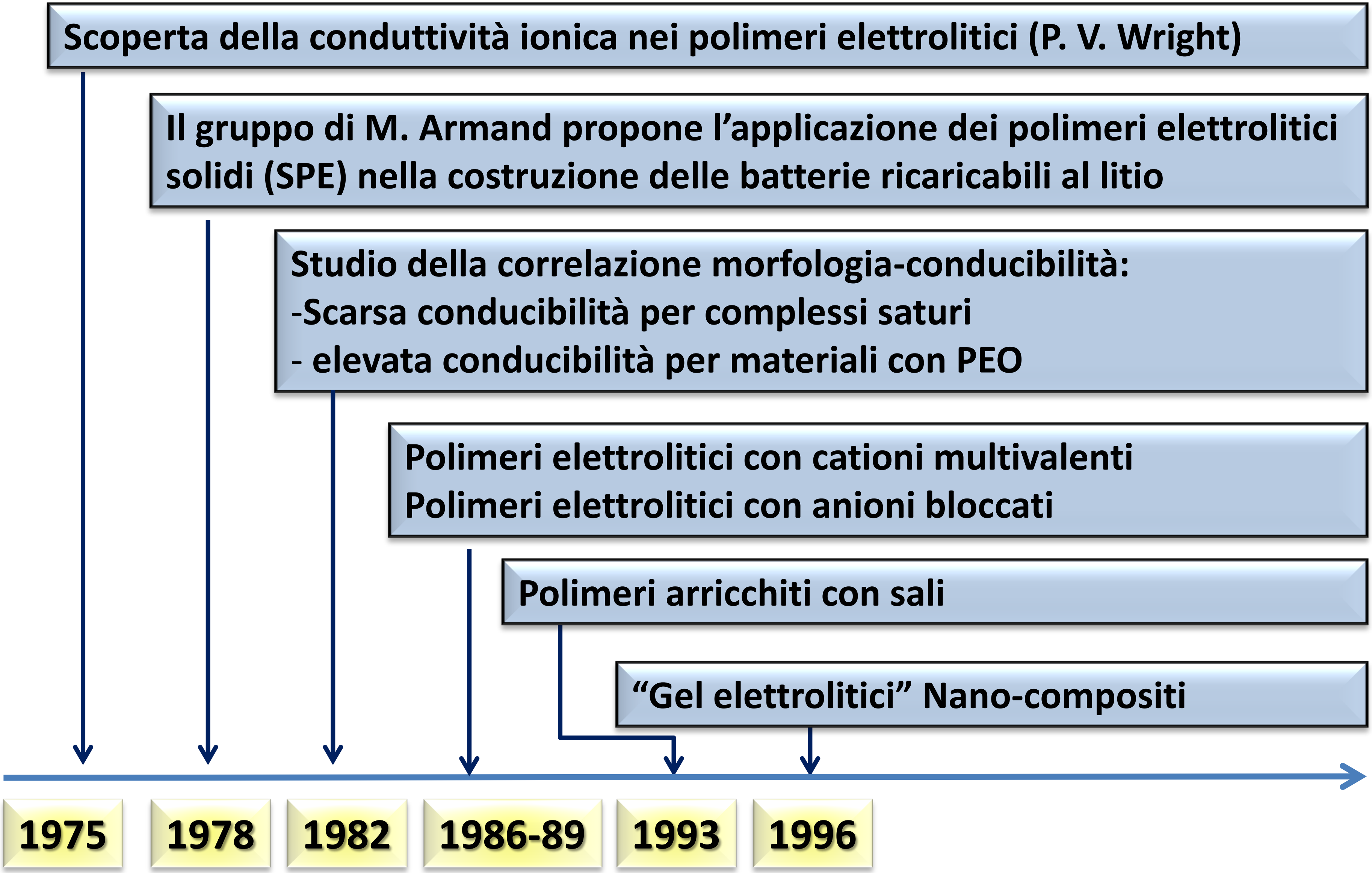
Invenzione batterie Na-S βAl_2O_3

Commercializzazione batterie a base di Li-I per pacemaker

Invenz. Batt. Ricaric. SPE al Li Dimostrazione ciclabilità a Tamb delle batterie SPE al Li

Elettrolita solido

Evoluzione dei Polimeri Elettrolitici



Scoperta della conduttività ionica nei polimeri elettrolitici (P. V. Wright)

Il gruppo di M. Armand propone l'applicazione dei polimeri elettrolitici solidi (SPE) nella costruzione delle batterie ricaricabili al litio

Studio della correlazione morfologia-conducibilità:
-Scarsa conducibilità per complessi saturi
- elevata conducibilità per materiali con PEO

Polimeri elettrolitici con cationi multivalenti
Polimeri elettrolitici con anioni bloccati

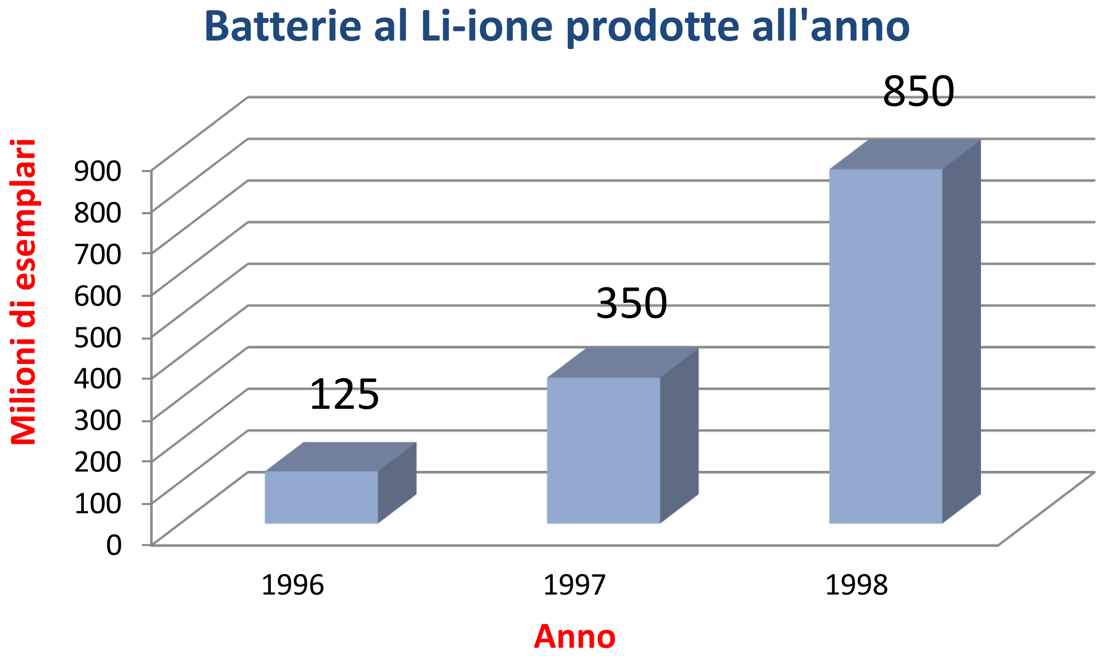
Polimeri arricchiti con sali

"Gel elettrolitici" Nano-compositi

1975 **1978** **1982** **1986-89** **1993** **1996**

Stato dell'arte di celle ricaricabili per elettronica portatile

	Ni-Cd	**Ni-MH**	**Li-ione**
Potenziale di scarica [V]	1.2 – 1.0	1.2 – 1.0	3.7 – 3.0
Energia specifica [Wh/g]	60 – 85	80 – 100	90 – 120
Densità di energia [Wh/l]	140 – 180	240 – 300	300 – 380
Costo energetico [$/Wh] (franco fabbrica)	0.3	0.4	0.8
Costo per ciclo [$/ciclo]	0.06	0.1	0.08 – 0.05
Cicli	1000	450	600 – 1000
Autoscarica (% mese)	15	20	12
Densità di potenza [W/l]	1000	800	500



- Una sorgente di potenza elettrochimica o batteria è un dispositivo che consente di convertire l'energia liberata in una reazione chimica in elettricità
- Le funzioni generali delle batterie sono:
  a) Sorgente portatile di potenza elettrica
  b) Sistemi di immagazzinamento reversibile di energia elettrica

Type	Energy	Applications
Miniature batteries	100 mWh – 2 Wh	Electric watches, calculators, implanted medical devices
Batteries for portable equipment	2 – 100 Wh	Flash-lights, toys, power tools, portable radio and television
SLI Batteries (starting, lighting and ignition)	100 – 600 Wh	Cars, trucks, buses, tractors, Lawn mower traction
Vehicle traction batteries	20 – 630 kWh (3 MWh)	Fork-lift Trucks, milk-floats, locomotive (Submarine)
Stationary batteries	250 kWh – 5 MWh	Emergency power supplies, local energy storage, remote relay stations
Load levelling batteries	5 – 100 MWh	Spinning reserve, peak shaving, load levelling

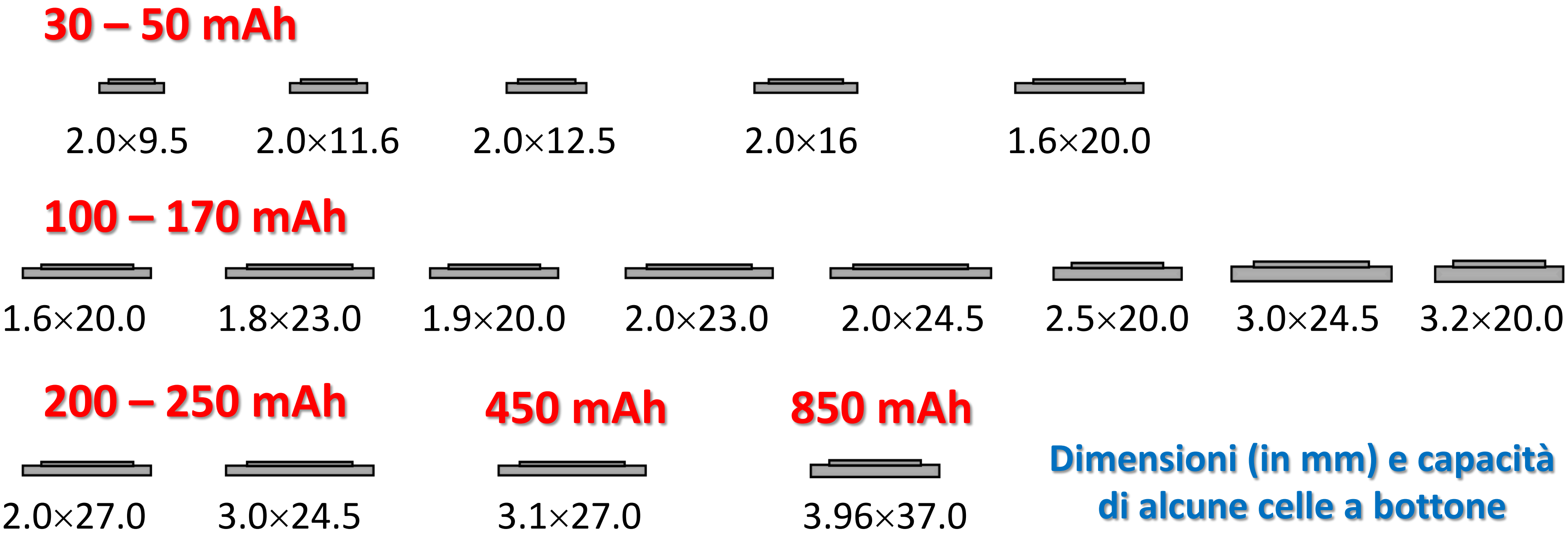
Batterie in miniature

Per microelettronica ed altri sistemi miniaturizzati, le batterie si distinguono per gli elettroliti impiegati:

A) acquosi;

B) Solidi;

C) Non acquosi



30 – 50 mAh

2.0×9.5 2.0×11.6 2.0×12.5 2.0×16 1.6×20.0

100 – 170 mAh

1.6×20.0 1.8×23.0 1.9×20.0 2.0×23.0 2.0×24.5 2.5×20.0 3.0×24.5 3.2×20.0

200 – 250 mAh

2.0×27.0 3.0×24.5

450 mAh

3.1×27.0

850 mAh

3.96×37.0

Dimensioni (in mm) e capacità di alcune celle a bottone

Batterie in miniatura

Orologi elettronici:

a. Circuito oscillante $0.2 \leq i \leq 0.6$ μA

b. Unità completa $0.5 \leq i \leq 2.0$ μA

Energia necessaria per far funzionare un orologio per un anno $\sim$ 15 – 60 mWh.

Requisiti per batterie in miniatura:

- bassa velocità di autoscarica;
- chiusura ermetica efficiente;
- basso volume

Possibili solo se esse presentano:

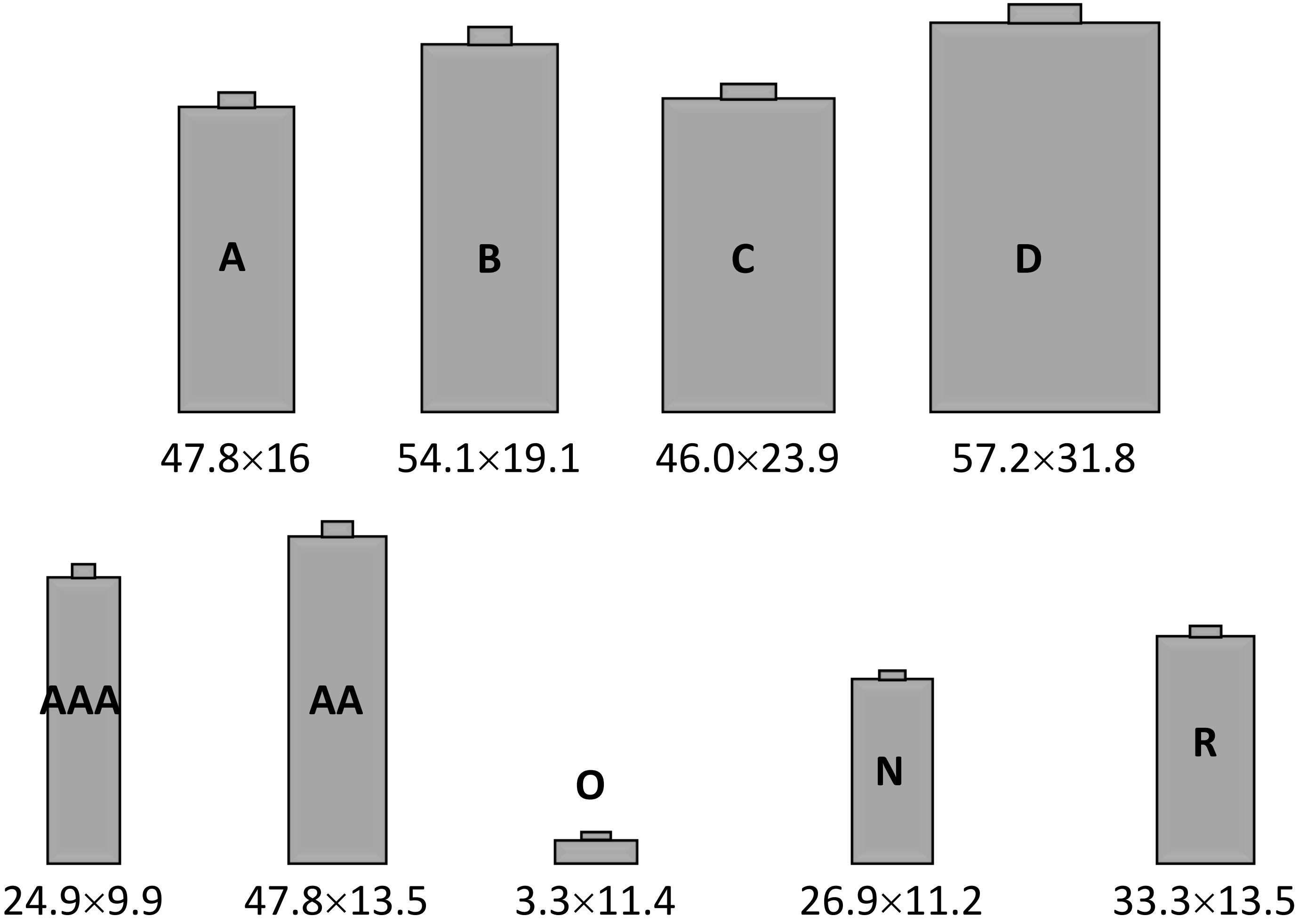
- elevata densità di energia
- buone caratteristiche della energia di scarica
- capacità di offrire impulsi di corrente occasionale

Pacemarker

Applicazione a pacemarker cardiaci

- 1960: primo pacemarker che pesano 200g e funzionano con batterie Zn-HgO (durata 1-3 anni)
- Oggi il pacemarker completo pesa 25g con un tempo di vita di almeno 10 anni (batteria al litio)
- Pacemarker intelligenti
- Tali sistemi domandano potenze molto basse:
  - 25-50 µW perla sensoristica
  - 60-100 µW per la stimolazione
- Ricerca: sviluppo batterie con alta velocità di scarica

Batterie per dispositivi portatili



Dimensioni standard (in mm) per batterie primarie a forma cilindrica

Batterie per dispositivi portatili

Primarie	**Ricaricabili**
Leclanché Zn – MnO_2	Alcaline: Nichel-Cadmio Ferro-Nichel ossido Ni-MH
Ruben – Mallory: Zn – HgO	Piombo-acide sigillate
Litio solvente	Capacità: 10 mAh – 15 Ah

Sono disponibili unità più grandi fino a 1000 Ah

Le ricaricabili alcaline sono interessanti perché presentano:
- **Buon numero di cicli di carica/scarica anche a bassa T;**
- **Ridotta velocità di autoscarica;**
- **buona modulazione del voltaggio;**
- **Sono robuste.**

? Costano più delle piombo-acide
? Bassa densità di energia

Batterie SLI
(shorting, lighting and ignition)

Servono per:

a) Accendere i motori ad alta compressione;

b) Per scintilla, illuminazione, ventilazione, etc…

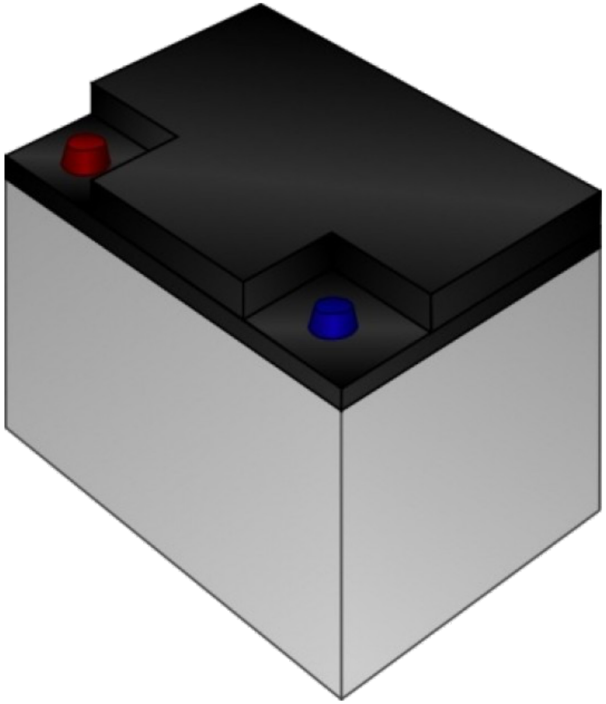
c) (batteria 12V costituita da 6 celle piombo-acida con capacità di circa 100Ah) circuiti elettrici automobilistici

SLI → $45\ \mathrm{Wh\cdot kg^{-1}}/75\ \mathrm{Wh\cdot dm^{-3}}$

SLI a Nichel-Cadmio con fogli di alluminio metallici sinterizzati molto sottili vengono usate quali sorgenti di potenza in aerei, elicotteri, cammionati, veicoli militari, etc…

I sistemi per aeronautica a 40 Ah possono fornire istantaneamente 20 kW di potenza a 25°C e circa 10 kW a -30°C (molto costosi).

Batterie per veicoli a trazione



- Una tipica automobile avente un peso a carico di 1 – 1.5 ton richiede 5 – 10 kWh di energia ogni 50 km percorsi. A tale scopo può consumare 4.5 dm^3 o 3.9 kg di benzina.
- Una batteria al piombo-acido in grado si essere ciclata in profondità di scarica fornisce 25 $Wh \cdot kg^{-1}$. Per far muovere l'automobile con tale sistema è necessario usare una batteria che pesa 200 kg e che occupa 120 dm^3.

Applicazioni batterie

In studio vi sono un certo numero di batterie innovative per EV.

Batterie operanti a T amb	a) Zn – Ni ossido	75 Wh·kg^{-1}
	b) Zn – Cl	80 Wh·kg^{-1}
Batterie operanti a T elevata	a) Sodio – Zolfo	120 Wh·kg^{-1}
	b) Zebra	160 Wh·kg^{-1}
	c) Litio – ferro solfuro	100 Wh·kg^{-1}

Veicoli elettrici ibridi

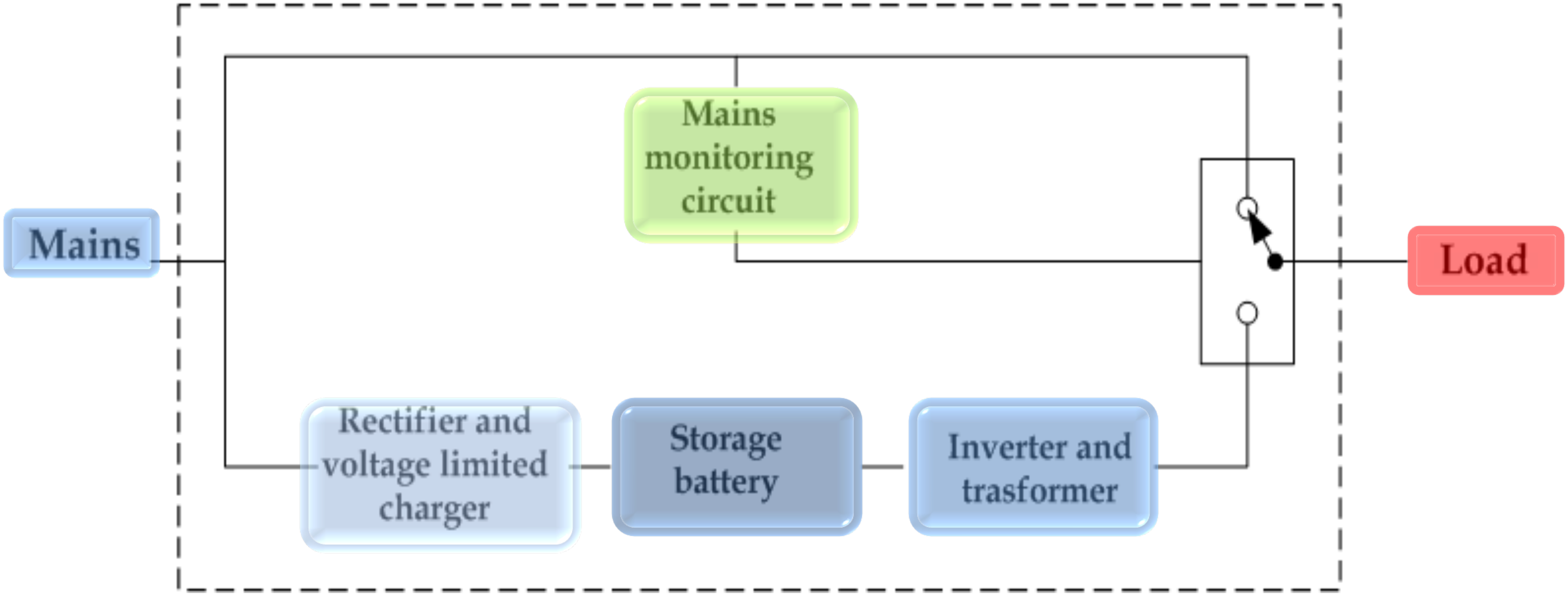
Batterie stazionarie

Potenza richiesta: 250 Wh – 5 MWh

Uso: - Luci di emergenza;
- Servizi telefonici;
- Ospedali, etc…

A tali sistemi molto raramente si chiede una profondità di scarica

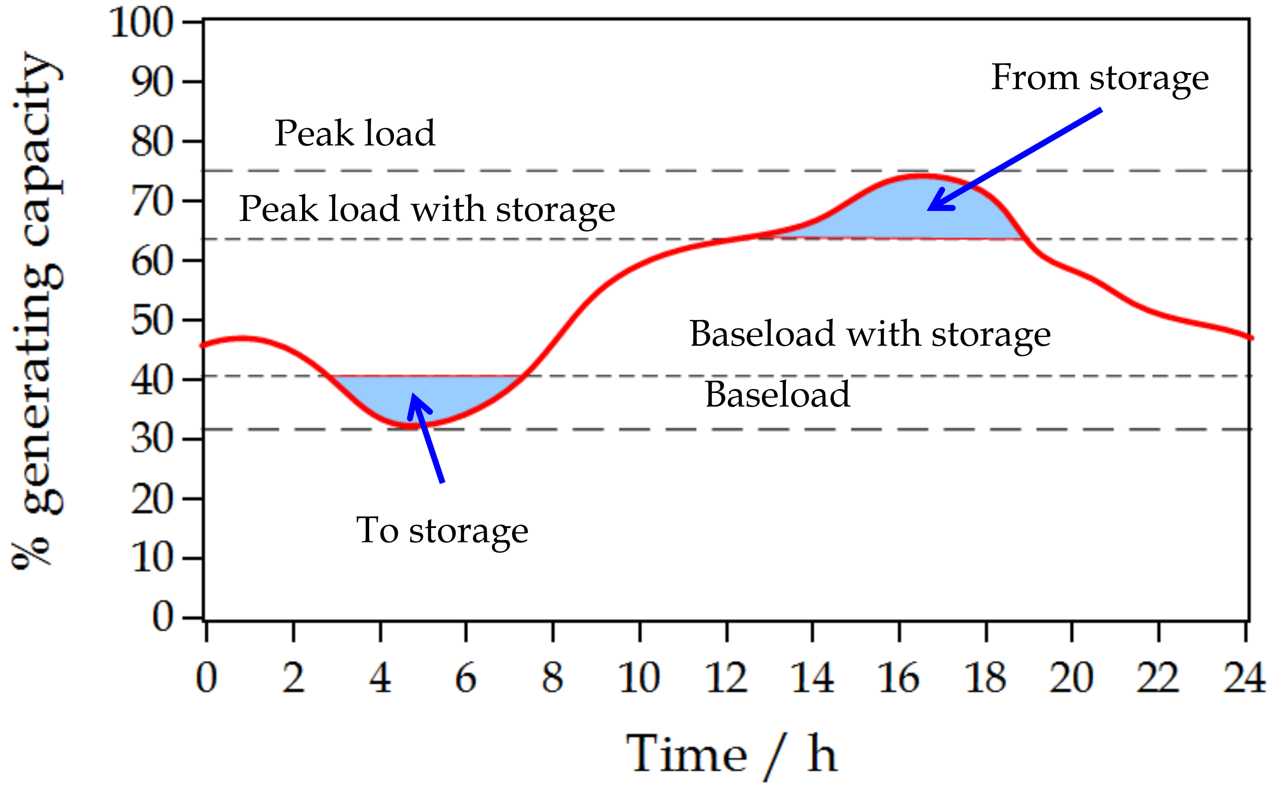
Applicazioni Batterie



Circuito schematico per un interruttore di emergenza

Batterie per immagazzinare energia elettrica da sistemi innovativi (400 Ah)
Batterie per livellamento di Carico

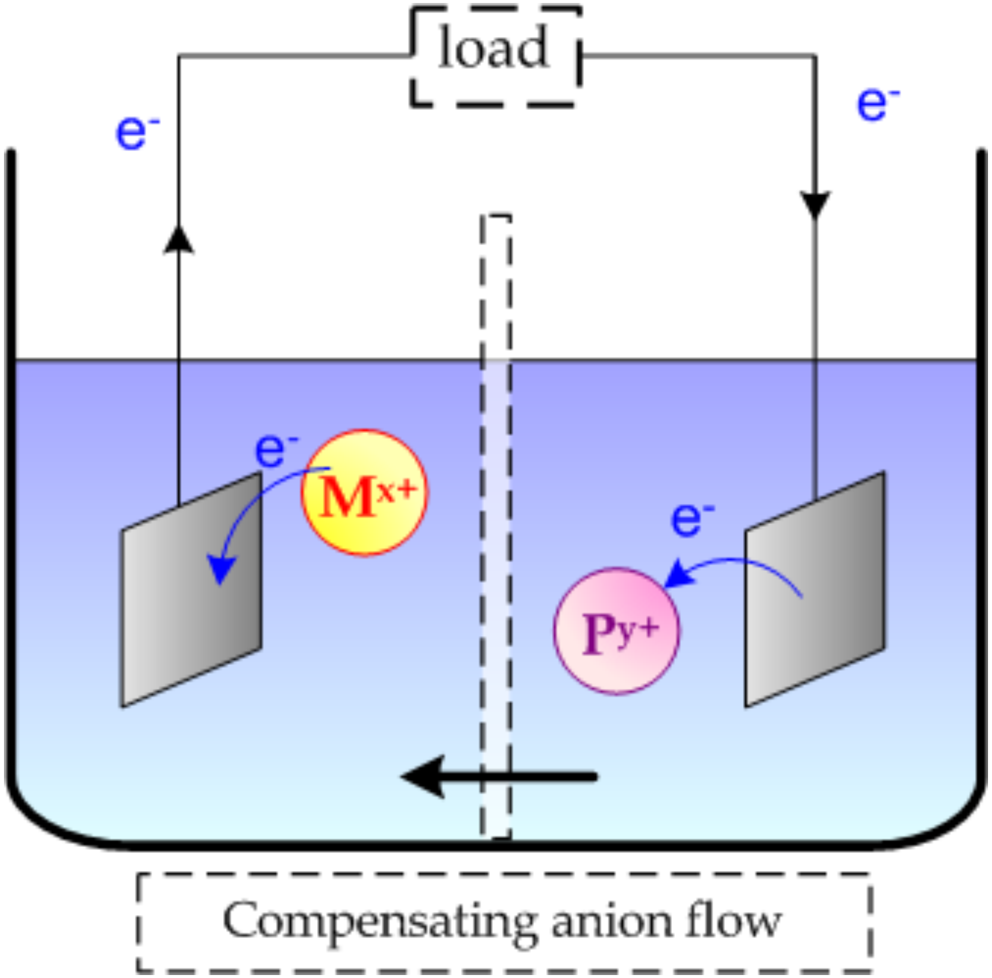
Batterie per livellamento di carico (200 – 2000 MWh)



National electricity demand curve. In the winter the curve moves up the y-axis: in the United Kingdom the winter demands is roughly double that of summer.

Basi elettrochimiche

$$M_{(aq)}^{x+} + P_{(aq)}^{y+} \rightarrow M_{(aq)}^{(x+1)+} + P_{(aq)}^{(y-1)+}$$



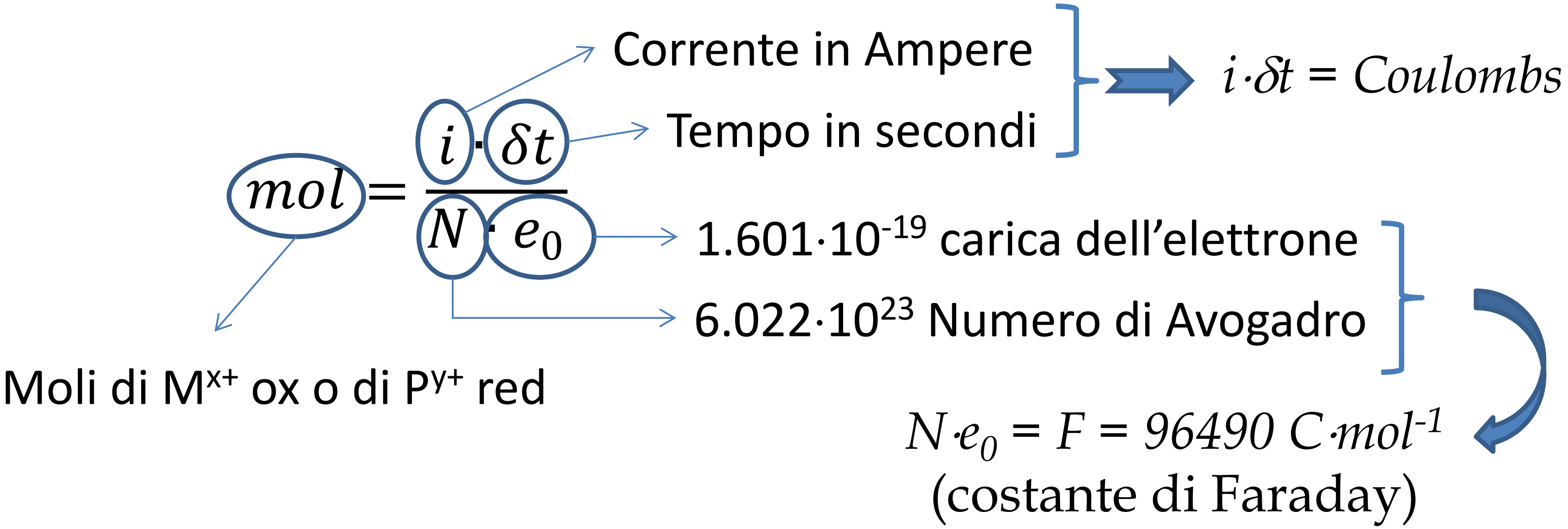
$\Delta G < 0$

- Reazione elettrochimica
- Processi elettrodici
- Il processo di cella è modulato dal ΔG della reazione

Interconnection of the two electrodes through the external load resistor allows the spontaneous cell reaction to proceed.

Prima legge di Faraday

La quantità di sostanza prodotta ad un elettrodo è proporzionale al flusso di corrente che è passato:



$$mol = \frac{i \cdot \delta t}{N \cdot e_0}$$

Corrente in Ampere

Tempo in secondi

$i \cdot \delta t = Coulombs$

$1.601 \cdot 10^{-19}$ carica dell'elettrone

$6.022 \cdot 10^{23}$ Numero di Avogadro

Moli di M^{x+} ox o di P^{y+} red

$N \cdot e_0 = F = 96490\ C \cdot mol^{-1}$

(costante di Faraday)

Processo elettrodico generale

$$M^{x+}_{(aq)} - \; ne^{-} \rightarrow M^{(x+n)+}_{(aq)}$$

Le moli di reagente consumate sono: $N_M = \dfrac{i \cdot \delta t}{nF}$

La corrente che attraversa una
cella può dipendere dal tempo

$$N_M = \frac{1}{nF}\int_0^t i\mathrm{d}t$$

$$Q_T = \int_0^t i\mathrm{d}t = nF \cdot N_M$$

La capacità massima di una cella (Q_T) è la quantità massima di carico che una cella può fornire al carico esterno

Il flusso di i·δt (Coulombs) nel catodo impone la riduzione all'anodo:

$$P^{y+}_{(aq)} + \; n'e^{-} \rightarrow M^{(y-n')+}_{(aq)} \quad \Rightarrow \quad N_P = \frac{i \cdot \delta t}{n'F}$$

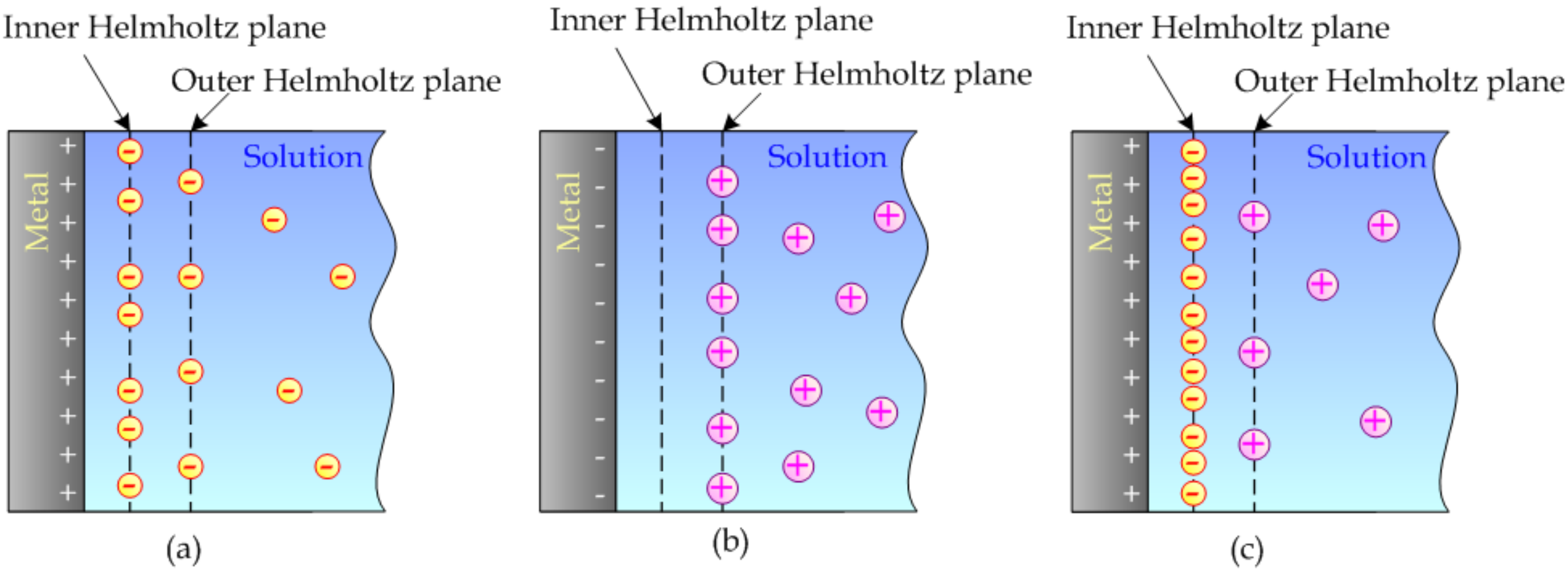
Moli di P^{y+} ridotte

Processo elettrodico generale

- La capacità massima di una cella che contiene N_M moli di M^{x+} ed N_p moli di P^{y+} è la più piccola i due valori: nFN_M e $n'FN_P$
- Se $nN_M = n'N_P$ si dice che la composizione della cella è perfettamente bilanciata. In teoria, i reagenti si esauriscono allo stesso tempo.
- Se $nN_M > n'N_P$ la cella si dice essere "limitata positivamente" o "limitata catodicamente": cioè, la massima quantità di carica che può essere usata in un circuito esterno è determinato da solo uno dei due componenti attivi, in questo caso P^{y+}.

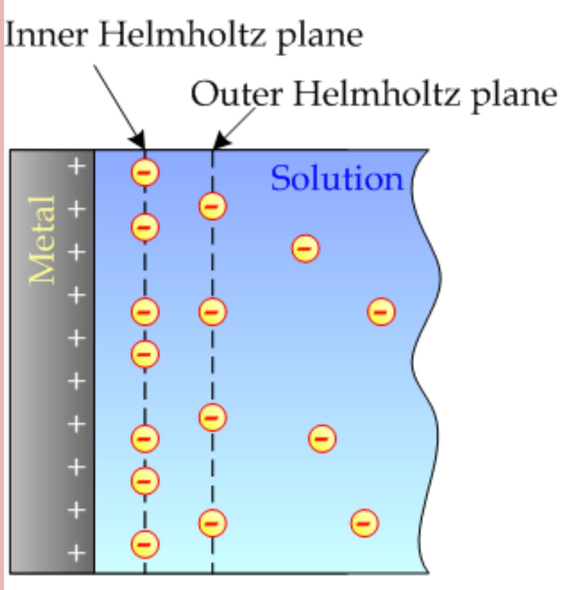
Di solito molte celle di uso corrente presentano questo problema

Doppio strato elettrico e formazione di potenziali elettrici alle interfacce



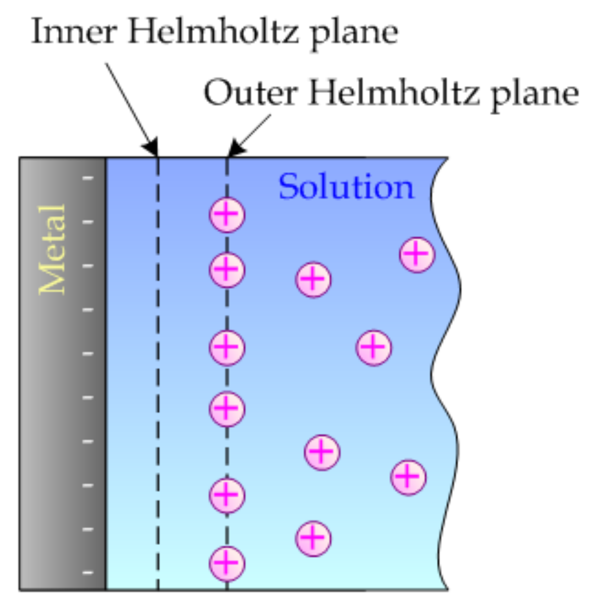
Structure of the electric double layer under different conditions of electrode polarization: a) metal positively charged, anions present at the inner Helmholtz plane (chemically interacting with metal) and in the diffuse double layer beyond the outer Helmholtz plane; b) metal negatively charged, inner Helmholtz plane empty, cations in diffuse layer; c) metal positively charged, strong adsorption of anions in inner Helmholtz plane, balancing cations in the diffuse layer

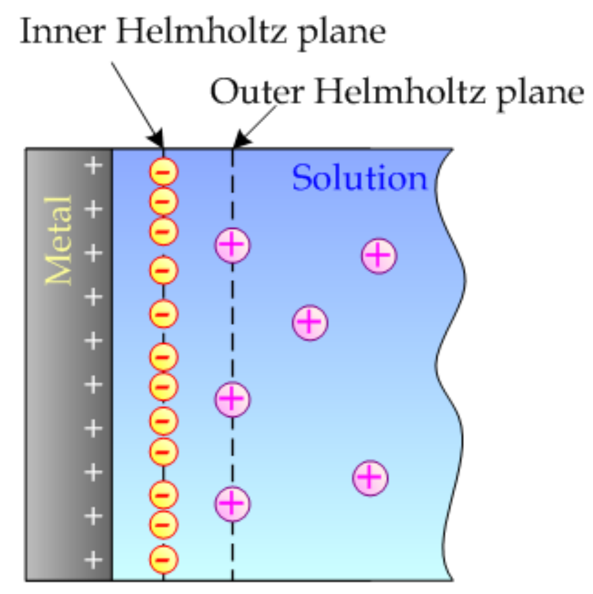
Doppio strato elettrico e formazione di potenziali elettrici alle interfacce



Metal positively charged, anions present at the inner Helmholtz plane (chemically interacting with metal) and in the diffuse double layer beyond the outer Helmholtz plane

Metal negatively charged, inner Helmholtz plane empty, cations in diffuse layer





Metal positively charged, strong adsorption of anions in inner Helmholtz plane, balancing cations in the diffuse layer

Structure of the Double Layer

The structure of the solution side of the double layer is much more complicated: it can be considered to consist in two regions:

a) An inner layer which may contain partially desolvated anions which have strong chemical bonding interactions with the metal together witn oriented solvent molecular dipoles

b) A "time average" diffuse layer where ions are attracted to or repelled from the interfaced by electrostatic forces, but which are also affected by thermal collsions. The effective depth of the diffuse layer is a function of electrolyte concnetration, temperature, dielectric constant of the solvent, etc…

The formation of an electric double layer at a metal-solution interface brings about a particular arrangement of ions in the region near the electrode surface and an associated variation in electric potetial with distance from the interface. The double layer structure may affect significantly the rates od electrochemical reactions.

Differenza di potenziale

In the case of electrochemical cells capable of passing significant direct currents, the principal mechanism for the formation of such potential differences at phase boundaries within the cell is charge transfer: e.g. electron transfer between two metals or semiconductors, ion transfer between metal and a solution of its ions, etc…

Esempio: un metallo inerte come il Pt immerso in una soluzione contenente la forma ossidata e ridotta di una specie chimica, per es. Fe^{3+} e Fe^{2+}.

1) all'inizio le due fasi separate sono cariche quindi non esiste tra loro differenza di potenziale;
2) quando le due fasi vengono a contatto possono succedere due cose:
   a) trasferimento di un elettrone dalla banda di conduzione del metallo al Fe^{3+}
   b) trasferimento di un elettrone da Fe^{2+} al metallo

Se la velocità dei processi (a) e (b) sono diverse le due fasi (metallo, soluzione) si caricano progressivamente

In particolare, se il processo (a) ha luogo più facilmente ben presto il metallo si carica positivamente e la soluzione negativamente sviluppando una differenza di potenziale (**ddp**).

Tale ddp influisce sulle velocità di trasferimento di carica

Il metallo carico (+) inibisce la riduzione di Fe^{3+} e favorisce l'ossidazione di Fe^{2+}

Così, al procedere dei trasferimenti di carica la ddp tra le fasi varia fino a quando le velocità dei processi

$$Fe^{2+} \xrightarrow{-e^-} Fe^{3+} \quad \text{and} \quad Fe^{3+} \xrightarrow{+e^-} Fe^{2+}$$

diventa uguale.

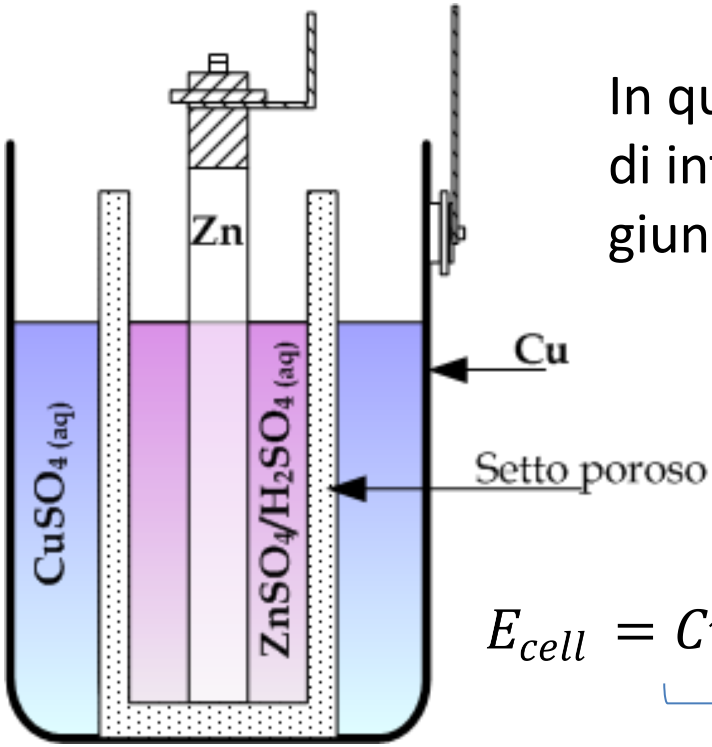
Differenza di potenziale all'equilibrio

In queste condizioni:

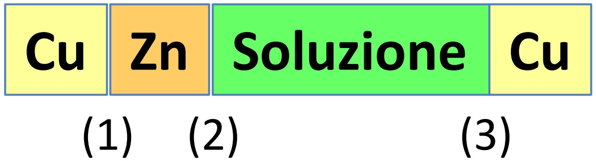
a) Uguale trasferimento di elettroni;
b) Si forma il doppio strato.

Two points may be made at this stage. First, the quantity of charge transferred between phases in order to establish an equilibrium potential difference is normally so small that the actual change in composition of the solution is negligible. For example, one can show that when a 1 cm^2 Pt electrode is immersed in a Fe^{2+}/Fe^{3+} solution, a net reduction of between 10^{-9} and 10^{-10} moles of Fe^{3+} takes place. Second, anc as will be stressed later, the kinetics of the charge transfer process are very important, since if rates are slow, it may not be possible for a true equilibrium to be establised.

Cella Daniel



In questo tipo di cella ci sono tre significativi ddp di interfaccia (si trascurano i piccoli potenziali di giunzione liquido)



Cu | **Zn** | **Soluzione** | **Cu**

(1) (2) (3)

$$\Delta = E^c - E^a$$

$$E_{cell} = \underbrace{Cu_\Delta Zn_\varphi}_{\cong 0.25\ \mathrm{V}} + Zn_\Delta Soluzione_\varphi + Soluzione_\Delta Cu_\varphi$$

The Galvani potential, ϕ of a phase defines the amount of electrical energy, $e\phi$, required to transport a charge e from an infinitely distant point in a vacuum to a hypothetical point in the interior of the phase where the charge would be experience no “chemical” forces exerted on it.

Unfortunately it is impossible to measure either the Galvani potential of a single phase or the Galvani potential difference between two phases of different composition. The only Galvani potential difference that can be measured in this cell is that existing between the two copper terminals.

Thus, it is not particularly instructive to develop further the concept of individual electric potenial differences at phase boundaries within a galvanic cell.

Instead, the relationship between the measurable cell voltage and the properties of the chemical processes associated with the running of the complete cell will now be considered.

Termodinamica di una cella

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$ **Reazione di Cella**

- Una cella si dice **reversibile** quando la reazione globale si inverte cambiando la direzione della corrente di cella.
- Quando non si ottiene più corrente si è all’equilibrio
- È da notare comunque che l’assenza di corrente non significa, necessariamente, che la cella sia all’equilibrio. Es:

$$2\mathrm{H}^{+}_{(\mathrm{aq})} + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2,(\mathrm{g})}$$

$$\mathrm{Fe}_{(\mathrm{s})} \rightarrow \mathrm{Fe}^{2+}_{(\mathrm{aq})} + 2\mathrm{e}^{-}$$

When no current is being drawn from a reversible cell, the potential difference across its terminals is known as the ***electromotive force*** or ***e.m.f.*** of the cell. The e.m.f. of any particular cell is a quantitative measure of the tendency of the cell reaction to occur and may be related to the free energy change for this process.

- The maximum work that may be obtained from the cell for one mole of reaction is:

$$w_{max} = nFE$$

- By definition, ***w_{max} = - ΔG,*** where ΔG is the free energy change associated with one mole of reaction and hence:

$$\Delta G = -nFE$$

- Galvanic cells can only supply electric work equal to the free energy change of the cell reaction when the current flowing tends to zero. The cell voltage under load is always smaller than the e.m.f. so that only part of the thermodynamically available work can be utilized.
- The enthalpy change associated with a cell reaction is a state function and hence is independent of whether the reaction is being carried out reversibly, the total enthalpy change ΔH will appear as heat given out to the surroundings:

$$\text{Heat given out} = q_{out} = -\Delta H$$

- On the other hand if some work is done by the cell (e.g. by turning an electric motor in order to lift a weight) then

$$w_{out} + q_{out} = -\Delta H$$

- The second law of thermodynamics determines how much work can be extracted from a process: for maximum work output there is an associated minimum heat output:

$$(w_{out})_{max} + (q_{out})_{min} = -\Delta H$$

- The term $(q_{out})_{min}$ may be identified with $-T\Delta S$ where ΔS is the entropy change of the cell reaction. If ΔS is positively, the cell will cool down as it operates, or take in heat from the surroundings. If the same cell operates irreversibly, it will cool down less, or take in less heat from the surroundings.

Rappresentazione di una cella

- Una cella si rappresenta scrivendo la composizione delle fasi individuali nell’ordine in cui esse sono collegate:
  - ✓ le zone di contatto di due soluzioni sono indicate da linee verticali doppie (potenziale di non equilibrio causato da separazione di carica dovuta a diversa velocità di diffusione ionica)
  - ✓ i confini tra fasi diverse sono indicati con linee verticali singole
- Convenzione di scrittura: **Le cariche positive nella cella devono migrare da sinistra a destra**

In questo modo il voltaggio di cella è uguale in segno e grandezza al voltaggio del terminale di destra, considerando quello di sinistra nullo.

$E_{cella} > 0$

- Se la reazione procede spontaneamente quando si collegano i due terminali:

$$Zn_{(s)}|Zn^{2+}_{(aq)}, m_1||Cu^{2+}_{(aq)}, m_2|Cu_{(s)}$$

$$m_1 = [Zn^{2+}] \qquad E_{\text{cell}} = +1.1V$$

$$m_2 = [Cu^{2+}]$$

ANODO (+) → CATODO

- Scarica spontanea: $Zn_{(s)} + Cu^{2+}_{(aq)}, m_2 \rightarrow Zn^{2+}_{(aq)}, m_1 + Cu_{(s)}$

$$Cu_{(s)}|Cu^{2+}_{(aq)}, m_2||Zn^{2+}_{(aq)}, m_1|Zn_{(s)}$$

$$E_{\text{cell}} = -1.1V$$

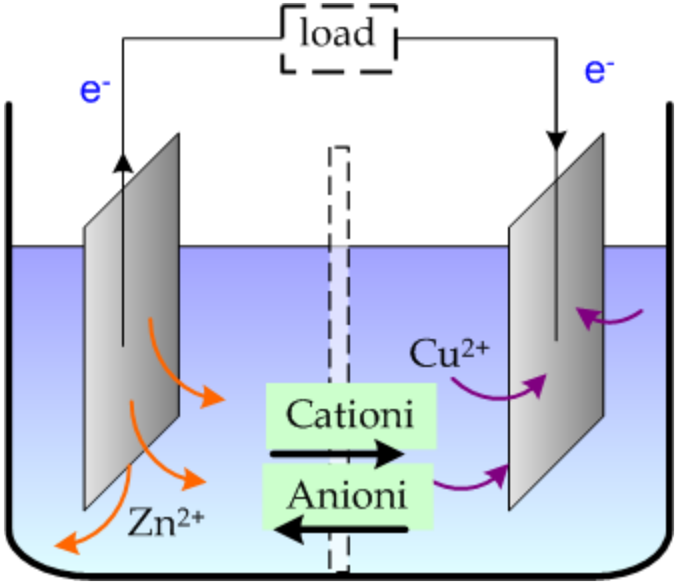
che descrive la non spontanea reazione di carico

$$Zn^{2+}_{(aq)}, m_1 + Cu_{(s)} \rightarrow Zn_{(s)} + Cu^{2+}_{(aq)}, m_2$$

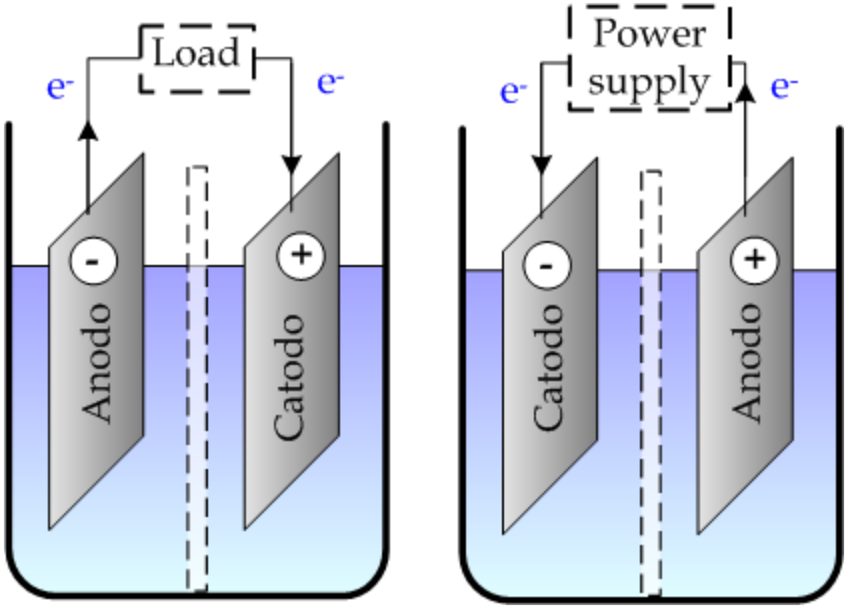
Flusso di elettroni in celle

In pratica per convenzione le celle galvaniche si scrivono nella reazione di scarica, quindi con l'elettrodo positivo sulla destra.

In questo caso, gli elettroni nel circuito esterno fluiscono da sinistra a destra e i catoni nella cella da sinistra a destra



Flusso di ioni ed elettroni in una cella Daniel



Anodo e catodo in una cella durante la scarica spontanea (sx) e durante la carica (dx)

- La dipendenza della e.m.f. di cella dalla concentrazione di reagenti e prodotti è di fondamentale importanza nella comprensione e nella progettazione di batterie per uso pratico.
- A mano a mano che la cella si scarica, i reagenti si convertono in prodotti fino a quando una delle specie dei reagenti sia completamente finita.
- Se si ha una reazione di cella: $A + B \rightarrow C + D$

  dove *A* e *D* sono specie in soluzione

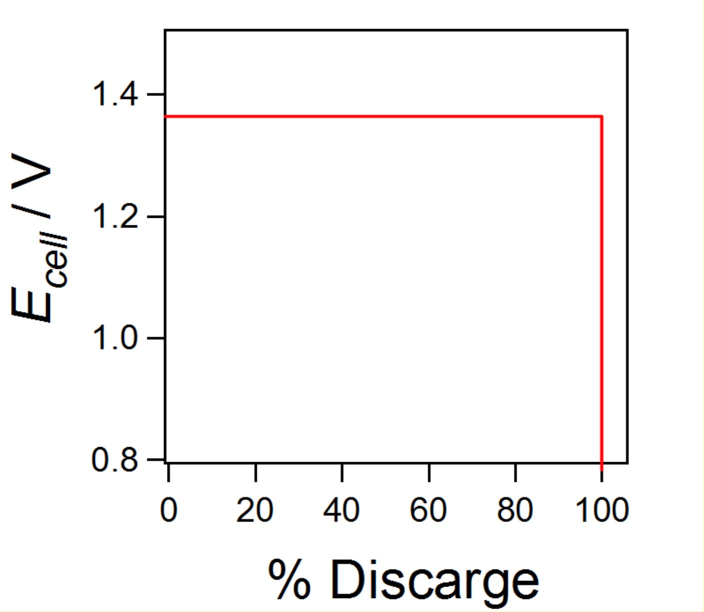
$$E_{cell} = E_{cell}^{0} - \frac{RT}{nF} \ln \left\{ \frac{a_C a_D}{a_A a_B} \right\}$$

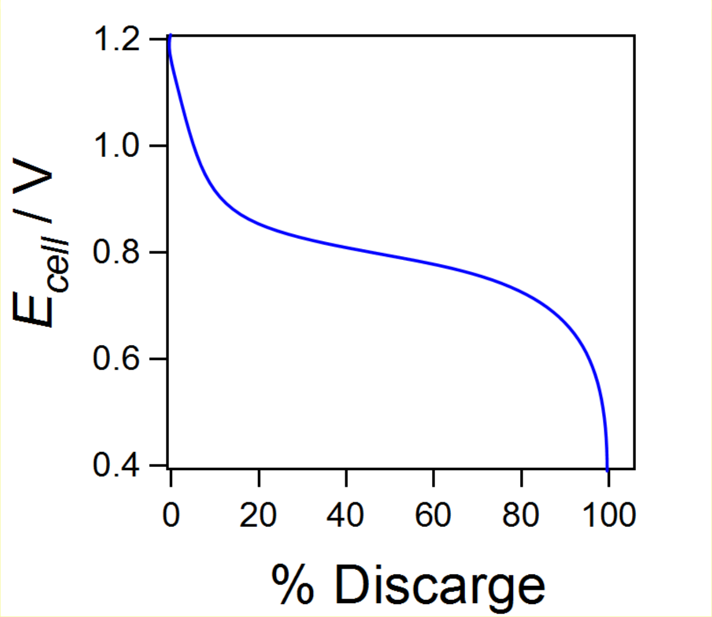
- A basse velocità di scarica la concentrazione dei reagenti è maggiore di quella dei prodotti: $E_{cell} \Rightarrow$ Valore elevato
- Con il procedere della scarica l'**OCV** (**Open Circuit Voltage**) controllato termodinamicamente diminuirà drasticamente.

- Se si vuole costruire una batteria che presenti una ridotta diminuzione di OCV in fase di scarica bisogna scegliere reagenti e prodotti la cui attività rimanga costante

$$Zn_{(s)}|ZnO_{(s)}|KOH_{(aq)}|\ HgO_{(s)}|Hg_{(l)}$$

$$Zn_{(s)} + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$$





$$Pt_{(s)}|Fe^{2+}_{(aq)}, Fe^{3+}_{(aq)}||Ce^{3+}_{(aq)}, Ce^{4+}_{(aq)}|Pt_{(s}$$

$$Fe^{2+}_{(aq)} + Ce^{4+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Ce^{3+}_{(aq)}$$

Open Circuit Voltage as function of percentage discharge for the cell

Dipendenza della e.m.f. dalla T e P

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p = -nFE$$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S \text{ or } \left(\frac{\partial \mathrm{E}}{\partial T}\right)_p = \frac{\Delta S}{\mathrm{nF}} \qquad \left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta V \text{ or } \left(\frac{\partial \mathrm{E}}{\partial p}\right)_T = \frac{-\Delta \mathrm{V}}{\mathrm{nF}}$$

- Dipendentemente dal segno della variazione dell’entropia associato alla reazione di cella si possono avere coefficienti di temperatura della e.m.f. positivi o negativi
- Tuttavia, a meno che nella cella non si sviluppi gas le variazioni di entropia e quindi di coefficiente di temperatura della e.m.f. sono molto piccoli.
- Una relazione pratica per stimare la dipendenza dalla temperatura è:

$$E_T = E_{298} + \frac{(T - 298)\Delta S}{nF}$$

T in K

Dipendenza della e.m.f. dalla T e P

- Per celle di stato solido si può supporre che e.m.f. non cambia con la pressione. Ma se si sviluppa gas:

$$E_p = E_{p^0} - \frac{1}{nF}\int_{p^0}^{p} \Delta V \mathrm{d}p$$

p^0 è la pressione standard

Esempio

$$Pt_{(s)}, H_{2,(g)}, p \left| HCl_{(aq)}, m \right|\left| AgCl_{(s)} \right| Ag_{(s)}$$

$$^1/_2\, H_{2,(g)} + AgCl_{(s)} \rightarrow H^+_{(aq)} + Ag_{(s)} + Cl^-_{(aq)}$$

$$\Delta V = -\,^1/_2\, \bar{V}_{H_2}$$

⇨ Volume molare H_2

$$\Delta V = -\,^1/_2 \frac{RT}{p}$$

Vale per pressioni < 10 atm, per p > 10 atm si usano relazioni più complicate

$$E_p = E_{p^0} + \frac{RT}{2nF}\int_{p^0}^{p} \frac{\mathrm{d}p}{\mathrm{p}} = E_{p^0} + \frac{RT}{2nF}\ln p$$

Valutazione indiretta dei potenziali di cella

- Bisogna sottolineare che a causa delle limitazioni cinetiche parecchie reazioni di semicella non possono essere usate per individuare possibili e.m.f. di celle pratiche

- Calori parziali molari ed entropie delle specie coinvolte sono determinati mediante metodi calorimetrici. Tali valori possono essere usati per ottenere ΔG^0 per la reazione di cella.

→ Da ΔG^0 si può calcolare facilmente E^0_{cella}.

Esempio

Si vuole calcolare E^0 del seguente processo

$$2\mathrm{CO}_{2,(g)} + 2\mathrm{H}^+_{(aq)} + 2e^- \rightarrow \mathrm{H}_2\mathrm{C}_2\mathrm{O}_{4,(aq)}$$

$$\begin{array}{c}
2\mathrm{CO}_{2,(g)} + 2\mathrm{H}^+_{(aq)} \xrightarrow{2e^-} \mathrm{H}_2\mathrm{C}_2\mathrm{O}_{4,(aq)} \\
\mathrm{H}_{2,(g)} \xrightarrow{-2e^-} 2\mathrm{H}^+_{(aq)} \\
\hline
2\mathrm{CO}_{2,(g)} + \mathrm{H}_{2,(g)} \rightarrow \mathrm{H}_2\mathrm{C}_2\mathrm{O}_{4,(aq)} \\
\hline
\end{array}$$

Se le energie di formazione dell’acido ossalico e della CO$_2$ sono conosciute:

$$\Delta G^0 = \left(\Delta G_f^0\right)_{H_2C_2O_4} - 2\left(\Delta G_f^0\right)_{CO_2} - 0$$

$$= (-695.0) - 2(-395.3) = +95.6\ kJ \cdot kmol^{-1}$$

$$E^0_{cell} = \frac{\Delta G^0}{nF} = -0.495\ \mathrm{V}$$

Flusso di corrente in una cella elettrochimica

Relazione corrente ↔ velocità di reazione

In una cella in carica o in scarica si possono considerare almeno tre forme di migrazione di carica:

i) Movimento degli elettroni (materiali elettrodici, connettori terminali, resistenza di carico, etc….)

ii) Flusso ionico nell’elettrolita (soluzioni acquose, elettrolita solido, Sali fusi, etc…)

iii) Reazioni di trasferimento di carica alle interfacce elettrodo/elettrolita (es. $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$)

Allo stato stazionario vi è neutralità in ogni parte macroscopica del sistema (cioè in ogni ***cross section*** del circuito di flusso totale di carica deve essere sempre lo stesso)

Rate of electron flow in external circuit = rate of charge transfer at each electrode/electrolyte interface

For the general electrode process

$$Ox + ne^{-} \rightarrow Red$$

nF coulombs are required to reduce one mole of Ox, so that the rate of reduction of Ox at the electrode is given by:

$$\left\{\frac{rate\ of\ passage\ of\ electrons\ into\ electrode\ from\ external\ circuit}{nF}\right\}$$

i.e.: rate of reduction of Ox [mol/s] is $\frac{\mathrm{d}n_{Ox}}{\mathrm{d}t} = \frac{1}{nF} \cdot \frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{1}{nF} \cdot i$

At the other electrode:

$$Red^{'} - n'e^{-} \rightarrow Ox'$$

and again, the rate of oxidation of Red' is: $\frac{\mathrm{d}n_{Red^{'}}}{\mathrm{d}t} = \frac{1}{n'F} \cdot \frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{1}{n'F} \cdot i$

- "***Current limiting process***" è quel processo che non è in grado di mantenere una velocità di flusso elettronico alto come tutti gli altri.
- Quali siano i fattori responsabili della velocità di flusso elettronico in cella?

Gli argomenti termodinamici sono in grado di predire la fattibilità del processo ma non la velocità di reazione.

Nella cella Daniel, all'equilibrio i trasferimenti di carica all'interfaccia Zn/soluzione sono:

$Zn^{2+}_{(aq)} \xrightarrow{2e^-} Zn_{(s)}$ ⇒ Flusso catodico i_c

$Zn_{(s)} \xrightarrow{-2e^-} Zn^{2+}_{(aq)}$ ⇒ Flusso anodico i_a

Hanno luogo alla stessa velocità!

All'equilibrio: $i_c = i_a = i_0$ ⇒ **Corrente di scambio**

in questo caso $i = i_c - i_a = 0$

Allo stesso modo all'elettrodo **Cu**: $i_c^{'} = i_a^{'} = i_0^{'}$

- Se si impone un potenziale alla cella in modo che il potenziale dello Zn sia meno negativo e quello del Cu meno positivo rispetto al valore di equilibrio

➡ In queste condizioni lo Zn è più facile da ossidare e rende più difficile la sua riduzione.

➡ $$i_a > i_c$$

$$|i_{Zn}| = i_c - i_a \neq 0$$ **Corrente anodica**

All’elettrodo di Cu, si favorisce la riduzione di Cu2+ e si inibisce l’ossidazione di Cu:

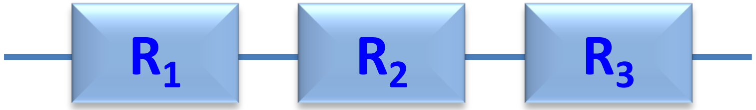
$$i_c > i_a$$

$$|i_{Cu}| = i_c - i_a \neq 0$$ **Corrente catodica**

Per mantenere la continuità di flusso di corrente:

$$|i_{Zn}| = |i_{Cu}| = \left|i_{flusso \ \ di \ \ ioni}\right|$$

Il voltaggio si distribuisce come nel caso si un potenziale, *E*, applicato a tre resistori in serie



$$\boxed{i = \frac{E}{R_1 + R_2 + R_3}}$$

$$\boxed{E_1 = \frac{E \cdot R_1}{R_1 + R_2 + R_3}}$$

Per scariche spontanee, il voltaggio di cella totale diminuisce rispetto al suo valore di equilibrio.

Se alla cella si applica una **d.d.p.** > **e.m.f.** (catodo più positivo e l'anodo più negativo) si osserva una corrente che fluisce in senso contrario.

Dissipazioni per polarizzazioni

- Knowledge of the amount by which the voltage of a cell, delivering a particular level of current, deviates from its equilibrium value is of central importance in assessing the performance of a pratical battery system.
- Il voltaggio di polarizzazione, E_p, è associato a due cause principali:

  i. caduta “Ohmica” o “iR” nell’elettrolita in bulk, separatori e qualche volta nella fase elettrodica e nei collettori;
  ii. caduta all’elettrodo, “sovratensione di attivazione”, dovuta a:

     a) trasferimento di carica;
     b) nucleazione e cristallizzazione;
     c) interfaccia elettrodo/elettrolita;
     d) sovratensione di concentrazione (perdita o accumulo di materiale elettroattivo in prossimità dell’elettrodo)

Dissipazioni per polarizzazioni

- Nelle batterie ad uso pratico, specialmente quelle che impiegano fasi porose non è sempre possibile separare, in modo chiaro, le cadute ohmiche ed elettrodiche.
- Per una cella in scarica:

$$E_{cell} = E_{termodinamico} - E_{pol}$$

- Per una cella in carica:

$$E_{cell} = E_{termodinamico} + E_{pol}^{'}$$

Caduta ohmica di potenziale

$$E_{ohmica} = i \sum_{j} \left(\frac{x_j}{A_j \sigma_j} \right)$$

Causa: resistenza interna della fase in bulk all’interno della cella

Caduta ohmica di potenziale

- Per una fase con conducibilità σ ($S \cdot cm^{-1}$) , la resistenza è:

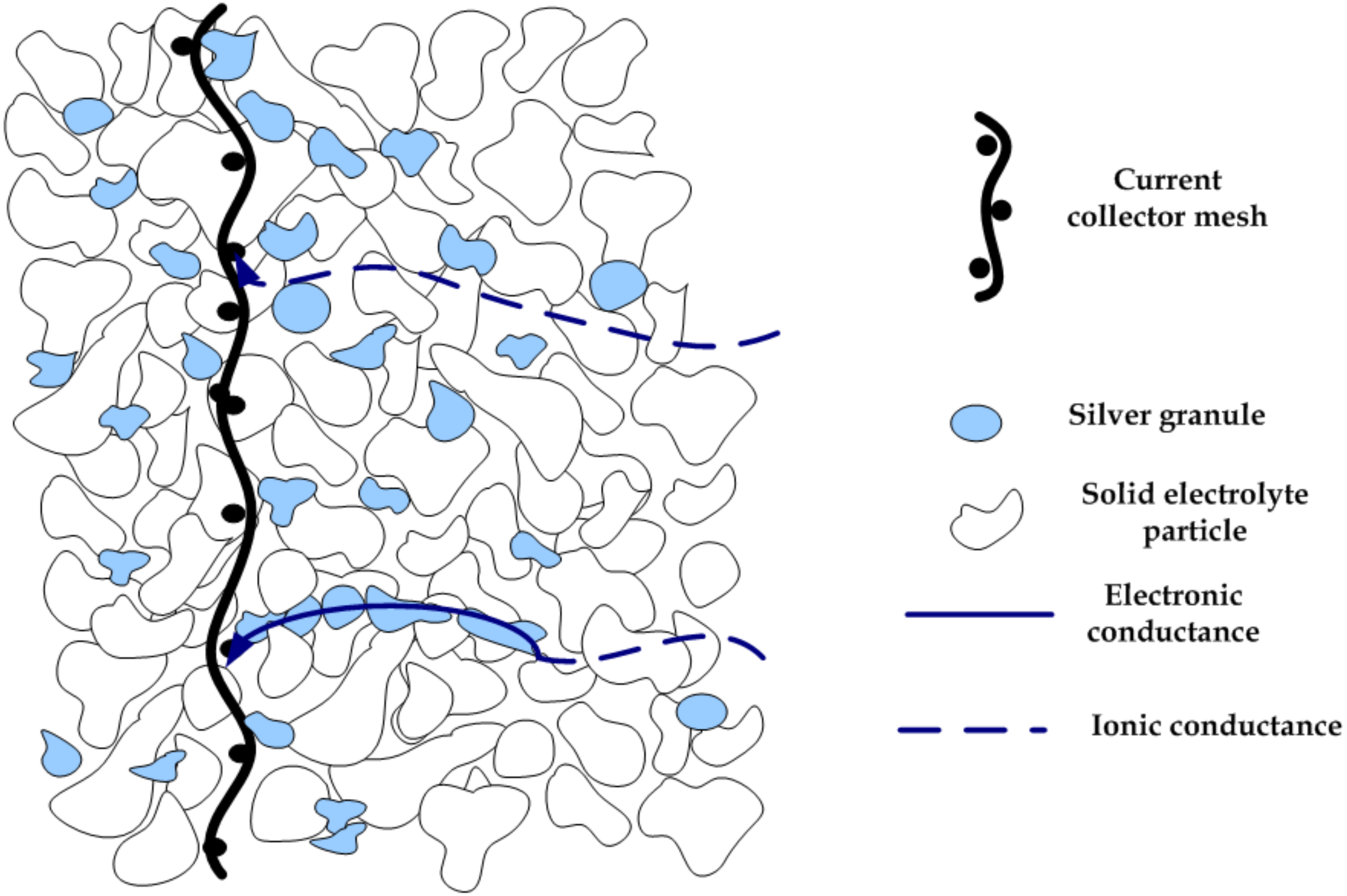
$$R = \frac{x}{A\sigma}$$

- Per il passaggio di una corrente **i** attraverso una cella con *j* fasi sequenziali.
- In pratica è impossibile avere distribuzioni di corrente uniforme che dipendono dalla geometria e dalle caratteristiche delle superfici elettrodiche

R_{ohmica} si può misurare mediante tecniche di perturbazione transienti

In many situations it is difficult to distinguish ohmic and electrode polarization, for instance where the electroactive material is also responsible for carrying all current in the electrolyte phase, in the situation where porous electrodes are involved, or where electrode and electrolyte phase are finely mixed, as in some solid-state cells.

Current patways in solid state cell



The electrode consist of granular silver metal and solid electrolyte

Caduta ohmica di potenziale

Two different conduction pathways are shown in a cell where the electrode material is granular silver ground together with a silver ion conducting solid electrolyte powder, and compressed to minimize electrode polarization by forming a large interfacial contact area. A very similar situation occurs with a porous electronically conducting electrode substrate and a liquid solution electrolyte.

It is common in many practical battery designs to ‘immobilize’ a liquid electrolyte phase within a porous solid insulator.

The electrolyte conductivity and ohmic loss in such system is determined by the number of pores, their size, shape and tortuosity.

The ***tortuosity coefficient***, β, is defined as the ratio of mean distance covered by an ion traversing a porous matrix, to the direct distance of one side of the matrix to the other.

Caduta ohmica di potenziale

The relative reduction in the conductivity of an electrolyte solution caused by confining it in a porous solid is called the **conductivity attenuation**, θ. For a matrix of uniform cylindrical pores it is given by

$$\theta = \frac{\pi N_p r_p^2}{\beta}$$

where $\boldsymbol{N_p}$ is the number of pores (with radius $\boldsymbol{r_p}$) per unit area of the solid matrix, and

$$\kappa_M = \theta \kappa$$

where $\boldsymbol{\kappa}$ is the conductance of the free electrolyte solution and $\boldsymbol{\kappa_m}$ is its conductance when immobilized.

In most modern pratical batteries, a major part of polarisation loss at moderately high current densities is due to ohmic potential drop. Considerable attention is therefore given during the design of a battery:

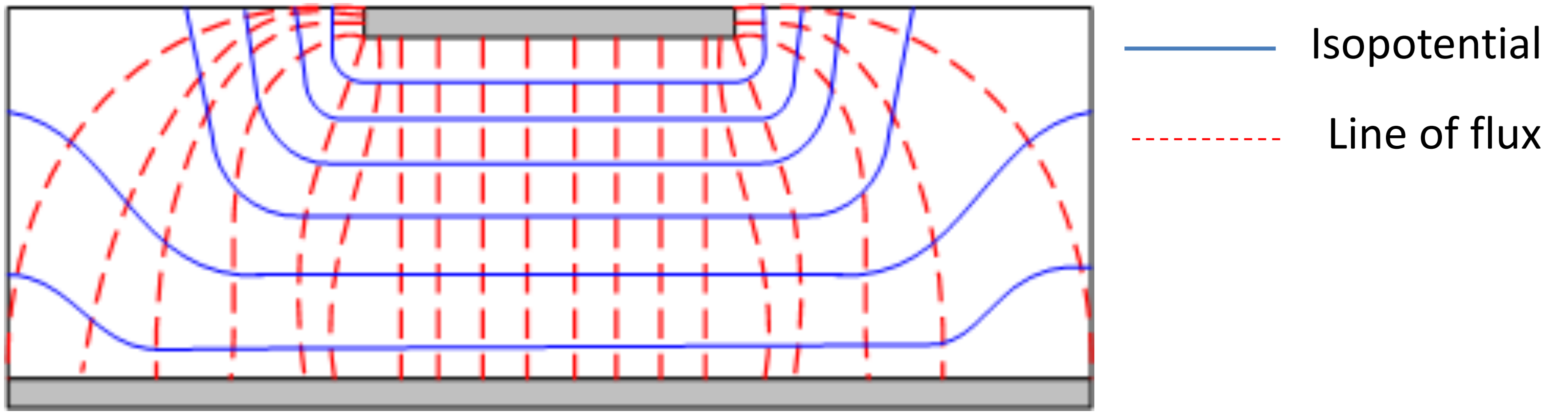
a) To obtain maximum ionic conductance in the electrolyte phases (a particular problem in certain non-acqueosu and solid electrolyte cells)

b) To reducing the resistivities of electrode materials (especially when they are in extended form, such as sintered powders, etc.) and suuplying adeguate current collectors, inter-cell connectors, etc…

c) To balancing the advantages from an electrode polarization viewpoint of high interfacial area against the drawback of high resistance paths in the bulk phases, and

d) To optimising cell geometry so as to minimise the effetive distance between electrodes, while maintaing uniform current distribution.

Uniform current distribution, is frequently of critical importance since variable current densities and associated non-uniform potential distribution can result in localized depletion of reactants, shape change in electrodes, side reactions, low reactions, low electrode material utilization, etc…



Cinetiche elettrodiche e caduta di polarizzazione elettrodica

La caduta di polarizzazione associata con un processo elettrodico è chiamata sovratensione

$$\eta = E - E_{eq}$$

$\boldsymbol{E_{eq}}$ è il potenziale a corrente Zero

E è il potenziale quando passa corrente

Un processo generale elettrodico può essere suddiviso in un numero di steps consecutivi:

- Trasporto di carica dell'elettrolita in bulk all'elettrodo
- Trasferimento di carica interfacciale

In some circunstances, one of the possible contributing factor to the overvoltage is sominant and it is possible to say that the electrode process is , for istance, ‘mass transport’ or ‘charge transfer’ limited. In other cases, more than one step is responsible for significantly restricting the current flow and overvoltage contributions from all such steps must be taken into account. Polarization losees of vaious kinds can sometimes be distinguished by subjecting the electrode to current or voltage transients (e.g. step or sinusoidal functions) and analysing the response.

Cinetiche di trasferimento di carica

Lo stadio di trasferimento di carica può coinvolgere:

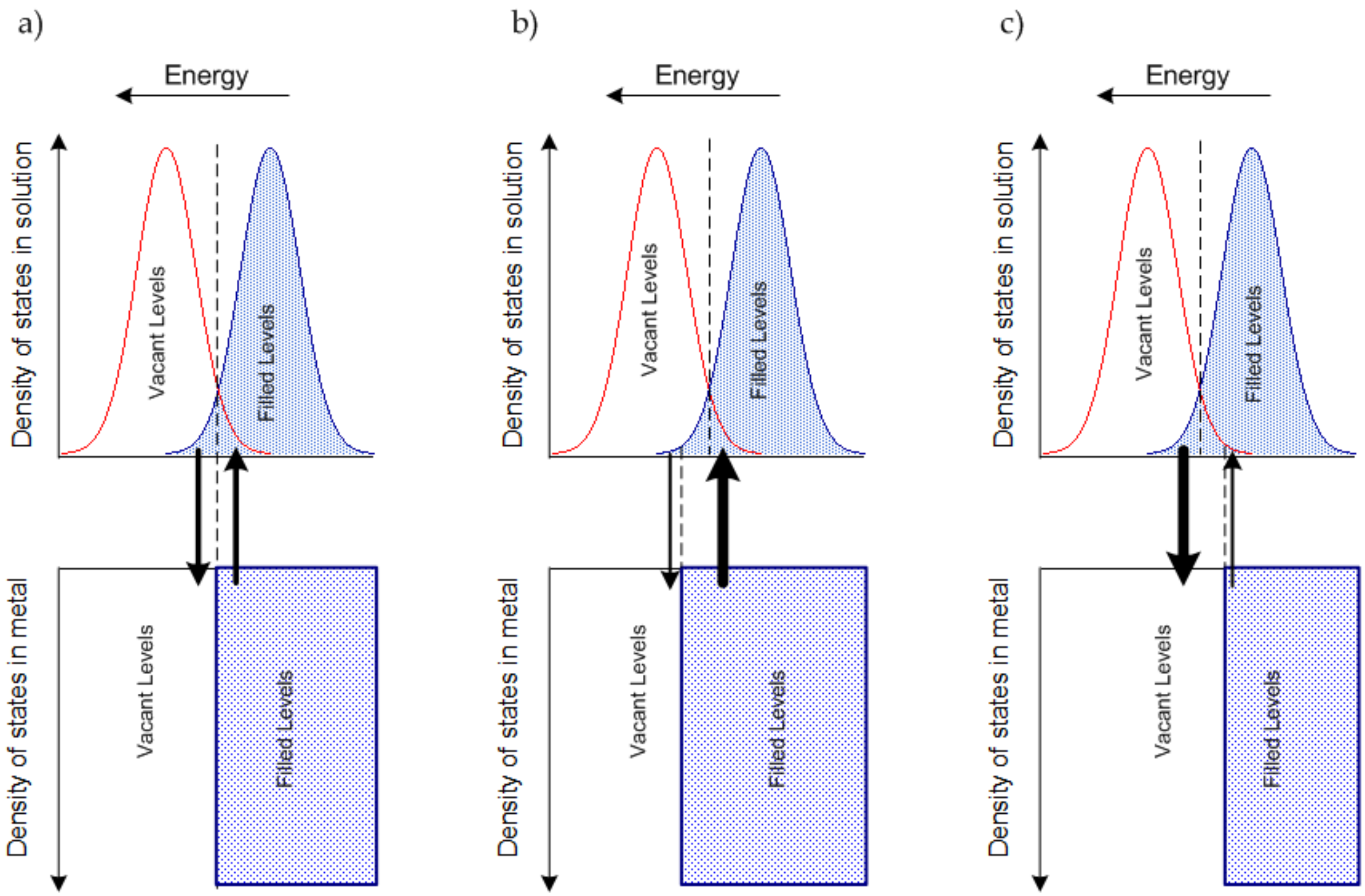
a) Trasferimenti elettronici $\mathrm{Pt_{(s)}|Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)}}$

b) Trasferimenti ionici $\mathrm{Zn_{(s)}|Zn^{2+}_{(aq)}}$

Anche se i trattamenti teorici dei due tipi di trasferimento di carica sono essenzialmente diversi in natura, le equazioni finali che legano la corrente e il voltaggio risultano molto simili.

Nel caso di elettrodi redox, la facilità con cui gli elettrodi passano attraverso una barriera di potenziale del tipo presente ad una interfaccia elettrodica rende non appropriato il trattamento del sistema mediante la teoria classica del complesso attivato (gli elettroni sono uno dei reagenti).

Occupation of energy levels in a metal and a solution redox couple



For all electron transfer between the phases to be successful, it is necessary for the acceptor or donor in solution to have an energy level exactly equal to a complementary level in the metal.

The current flowing at a redox electrode is not limited by the rate at which electrons can tunnel to or from the metal: rather, it is restricted by the rates at which the solution species can undergo thermal fluctuations to produce transient species (e.g. ions eith abnormal hydratation sheats, or molicules with streched bonds) which have suitable electronic states.

For the electrode process

$$Ox_{(aq)} + e^{-} \rightarrow Red_{(aq)}$$

The forward and reverse reactions can be considered as normal heterogeneous rate processes, but with rate constants which are potential dependent. Thus

$$i_c = k_c FA[Ox]$$
$$i_a = k_a FA[Red]$$

where k_c and k_a are heterogeneous rate constants, A is the area of electrode/solution interface and [*Ox*] and [*Red*] are the srface concentration of the eectroactive species – here assumed to be the same as the bulk values.

The rate constants have the form

$$k_c = k_0 exp\{-\alpha F\,(E - E^0)/RT\}$$
$$k_a = k_0 exp\{(1-\alpha) F\,(E - E^0)/RT\}$$

where E is the potential of the electrode, E_0 is its **standard** equilibrium potential and k_0 is the single heteregenous rate constant characteristic of the redox system at the temperature of interest. α is a constant between 0 and 1, known as the **transfer coefficient** or **symmetric factor**: its value is generally close to 0.5.

Se l'elettrodo è all'equilibrio:

$$\begin{aligned} i_0 = i_a = i_c &= k_0 FA[Ox]\exp(-\alpha F\,(E - E^0)/RT) \\ &= k_0 FA[Ox]\exp\{\ln([Ox]^{-\alpha}/[Red]^{-\alpha})\} \\ &= k_0 FA[Ox]^{1-\alpha}[Red]^{\alpha} \end{aligned}$$

Anche se la corrente netta è ZERO all’equilibrio, l’attività faradica può essere espressa in termini di **corrente di scambio, *i_0***.

All’equilibrio la corrente di scambio corrisponde in valore alla i_c ed i_a. Praticamente, la corrente di scambio è normalizzata all’unità di area fornendo così la ***Densità di corrente di scambio:***

$$j_0 = {}^{i_0}/_{A}$$

This general expression for the exchange current reduces to

$$i_0 = k_0 FA[Ox] = k_0 FA[Red]$$

for the situation where [*Ox*]=[*Red*], i.e. at the standard potential of the couple, and to

$$i_0 = k_0 FA$$

for the special case corresponding to the situation where $[Ox] = [Red] = 1$

Whenever there is a net flow of current, this is taken by convection as

$$i = i_c - i_a$$

For $i_c \neq i_a$, it is no longer strictly correct to equate the surface and bulk concentrations of the electroactive species. However if the charge transfer rate is current limiting, then as a first approximation it can be assumed that the surface concentration does not deviate significantly from the bulk value. Hence,

$$i = k_0 FA \Big[[Ox] \exp(-\alpha F\,(E - E^0)/RT) \\ - [Red] \exp\big((1-\alpha) F\,(E - E^0)/RT\big) \Big]$$

Also η=E-E_{eq}(E_{eq}=E^0+$RT/(nF)\cdot\ln[Ox]/[Red]$), so that

$$(E - E^0) = \eta + \frac{RT}{F} \ln \frac{[Ox]}{[Red]}$$

Hence on substituting for (E-E^0) and recalling the expression derived for i_0

$$i = i_0\{\exp(-\alpha F\,\eta/RT) - \exp\big((1-\alpha)F\,\eta/RT\big)\}$$

This equation is known as the **Buttler-Volmer relationship**.

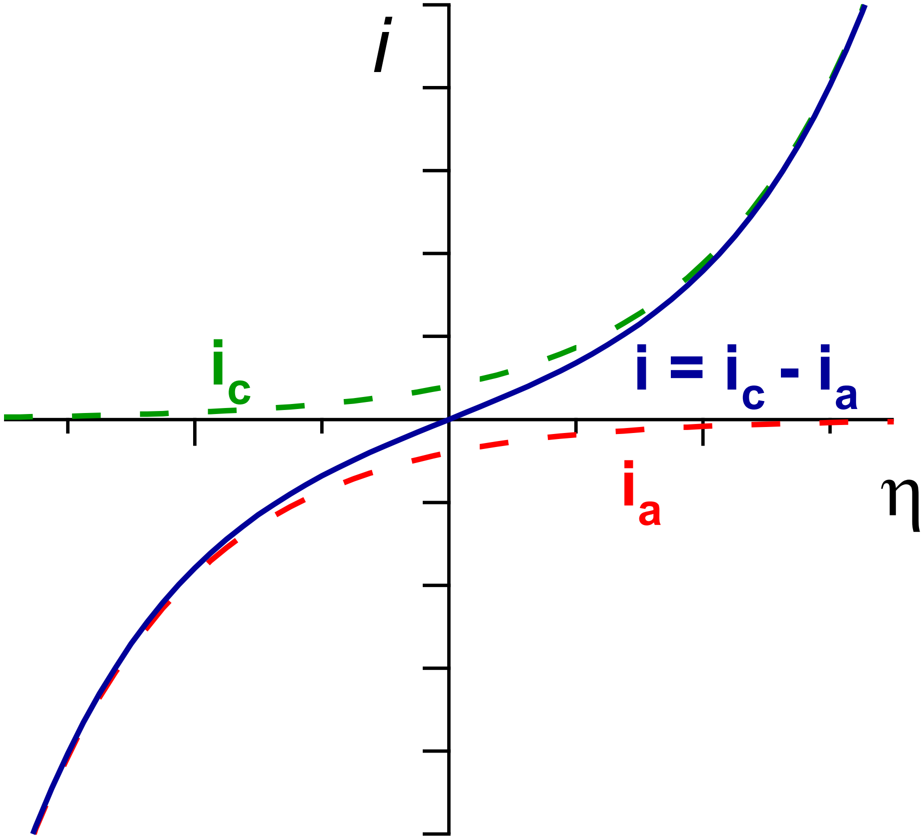
Generalizzando al caso in cui la concentrazione superficiale [Ox] e [Red] è diversa da quella in bulk [Ox]* e [Red]* e per *n* elettroni scambiati:

$$i = i_0\left\{\frac{[Ox]}{[Ox]^*}\exp\left(\frac{-\alpha nF}{RT}\eta\right) - \frac{[Red]}{[Red]^*}\exp\left(\frac{(1-\alpha)nF}{RT}\eta\right)\right\}$$

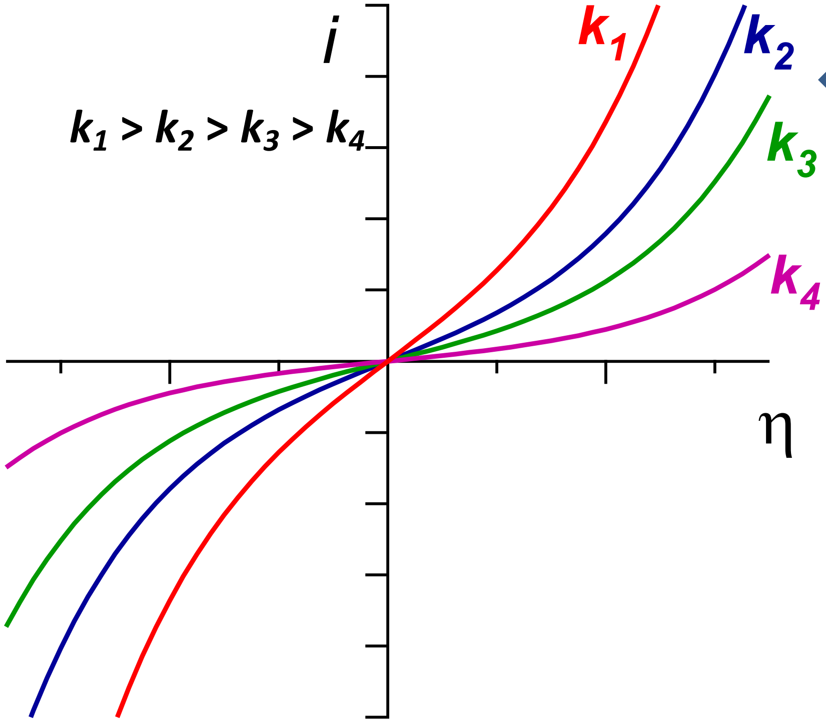
Current-overpotential equation

The net current flowing at an electrode can be considered as the resultant or sum of the cathodic and anodic contributions

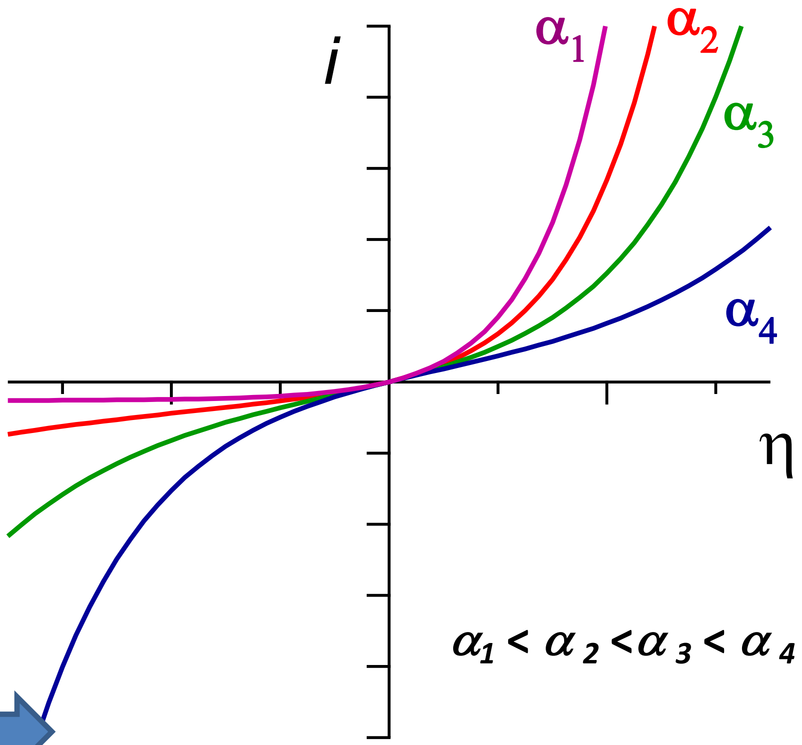
Net current flow, *i*, at an electrode as the resultant of cathodic and anodic contributions, i_c and i_a.



The exact shape of the curve is defined by two parameters k_0 and α.



It can be seen that if the heterogeneous rate constant is high, large curents can be generated by very small overvoltages



The variation of α for a constant k_0 is seen to alter the symmetry of the current/voltage behaviour.

An interesting feature of this profile is the coincidence of all curves near the origin: use can be mode of this for determining i_0.

The charge transfer resistance or polarization resistance R_p of electrode is defined as the inverse of the current/potential gradient at η=0:

$$R_p = \frac{1}{\left(\frac{\mathrm{d}i}{\mathrm{d}\eta}\right)_{\eta=0}}$$

The exchange current is a measure of any system’s ability to deliver a net current without a significant energy loss due to activation.

$$\frac{\mathrm{d}i}{\mathrm{d}\eta} = i_0 \left\{ \frac{-\alpha nF}{RT} \exp\left(\frac{-\alpha nF}{RT}\eta\right) - \frac{(1-\alpha)nF}{RT} \exp\left(\frac{(1-\alpha)nF}{RT}\eta\right) \right\}$$

$$\left(\frac{\mathrm{d}i}{\mathrm{d}\eta}\right)_{\eta=0} = i_0 \left\{ \frac{-\alpha nF}{RT} - \frac{(1-\alpha)nF}{RT} \right\} = -\frac{i_0 nF}{RT}$$

$$R_p = \frac{RT}{nFi_0}$$

This parameter can be evaluated directly in some experiments, and it serves as a convenient index of kinetic facility

For $k_0 >> \Rightarrow R_p \cong 0$

i_0 can therefore be found by taking the tangent to the current/potential curve at the origin. In practice, when η is small, the general expression for the current can be simplified by using the relationship:

$$\exp(-x) \approx 1 - x$$

Under these circumstances,

$$\boxed{i = -i_0 \frac{nF\eta}{RT}}$$

Determing the α and k_0 value

There are a number of methods available for determing α. For instance at equilibrium: $i_0/[Ox] = k_0 nFA([Ox]/[Red])^{-\alpha}$

$$\log\left(i_0/[Ox]\right) = \log(k_0 nFA) - \alpha \log([Ox]/[Red])$$

A plot of log($i0$/[Ox]) versus log([Ox]/[Red]) gives α from the slope.

The transfer coefficient may also be evaluated using a form of the Tafel equation as outlined below. If α and i_0 are known, then $\boldsymbol{k_0}$ is given as:

$k_0 = \dfrac{i_0}{nFA[Ox]^{1-\alpha}[Red]^{\alpha}}$	General Case
$k_0 = \dfrac{i_0}{nFA[Ox]} = \dfrac{i_0}{nFA[Red]}$	At the Standard potential of couple
$k_0 = \dfrac{i_0}{nFA}$	When [Ox]=[Red]=1

From the definition of ic and ia, we obtaine

$$\frac{i_C}{i_a} = \exp\left(-\frac{\mathrm{nF\eta}}{\mathrm{RT}}\right) \qquad \text{or} \qquad \log_{10}\left(\frac{i_C}{i_a}\right) = -\frac{n}{0.059}\eta \quad \text{at } 25°\mathrm{C}$$

Thus for an overvoltage of -118 mV, $i_c/i_a = 100/1$. for overvoltages of 200 mV and above, only the cathodic or anodic contribution to the total current need be considered. For a large cathodic overvoltage:

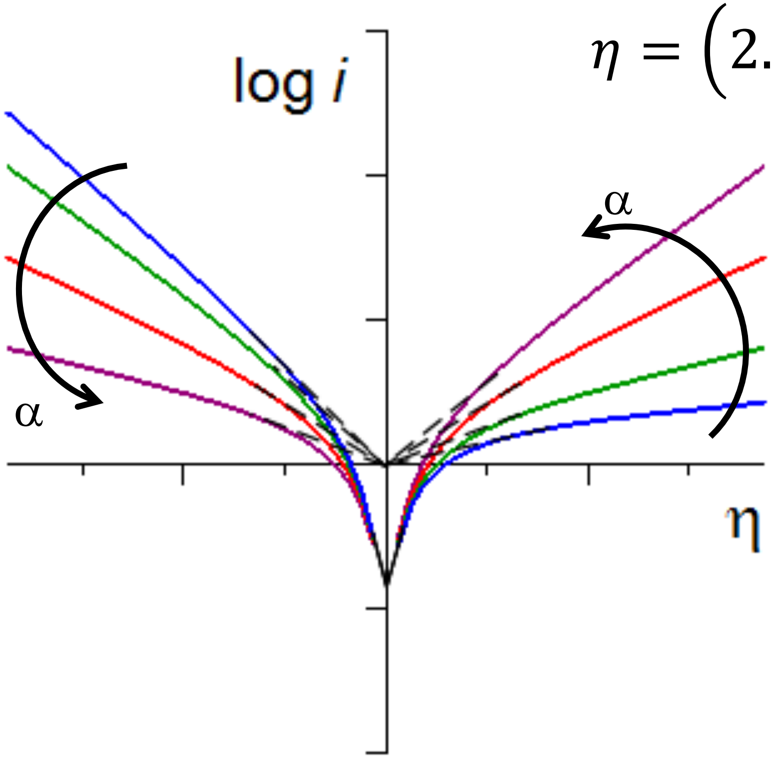
$$\begin{aligned} i &= i_c - i_a \\ &\approx i_c \\ &= i_0 \exp\left(-\alpha\frac{\mathrm{nF\eta}}{\mathrm{RT}}\right) \end{aligned}$$

⇒

$$\ln i = \ln i_0 - \alpha\frac{\mathrm{nF\eta}}{\mathrm{RT}}$$

Tafel plot

Plots of log *i* as a function of η: extrapolation of the linear portions of the curves to $\eta = 0$ gives the value of the exchanged current i_0, while α may be evaluated from their gradients.



$$\eta = \left(2.303\, {}^{RT}/_{\alpha nF}\right)\log i_0 - \left(2.303\, {}^{RT}/_{\alpha nF}\right)\log i$$

$$\underbrace{\eta = A + B\log i}$$

This equation is the usual form of the well-known **Tafel equation**. A similar expression exists for anodic currents.

Tafel plot is a useful device for evaluating kinetic parameters.

The negative deviations from linearity at very large overpotential come from limitations imposed by mass transfer

Tafel relationships cannot be observed for fairly facile electrode kinetics, because they require the absence of mass transfer effects on the current.

Where electrode kinetics are sluggish and significant activation overpotentials are required, good Tafel relationships can be seen. This point underscores the fat that Tafel behaviour is an indicator of totally irreversible kinetics. (Systems in that category allow no significant current flow except at high overpontetials)

Anodic charge transfer $M_{(s)} \rightleftharpoons M_{(ad)} \rightarrow M^{n+}_{(aq)} + ne^-$

Cathodic charge transfer $M^{n+}_{(aq)} + ne^- \rightarrow M_{(ad)} \rightleftharpoons M_{(s)}$

It is assumed that for pure charge transfer current limitation, the equilibrium between M(s) and M(ad) is fast and potential independent. Under these conditions the relevant equations are:

$$k_a = k_0 \exp\{(1-\alpha)nF\,(E-E^0)/RT\}$$

$$i_a = k_0 nFA\left[M_{(ad)}\right] \exp\{(1-\alpha)nF\,(E-E^0)/RT\}$$

$$k_c = k_0 \exp\{-\alpha nF\,(E-E^0)/RT\}$$

$$i_c = k_0 nFA\left[M_{(aq)}^{n+}\right] \exp\{-\alpha nF\,(E-E^0)/RT\}$$

$$i_0 = k_0 nFA\left[M_{(aq)}^{n+}\right]^{1-\alpha}\left[M_{(ad)}\right]^{\alpha}$$

and

$$i = i_0\left\{\exp\left(-\alpha\frac{nF\eta}{RT}\right) - \exp\left(\frac{(1-\alpha)nF\eta}{RT}\right)\right\}$$

Concentration overvoltage

- The term concentration overvoltage is used to describe restrinctions in the current caused by concentration changes of the electroactive species at the electrode surface
- In pratical, batteries such an effet is important at relatively high current densities.
- If attention is focused first on the electrolytic phase, it is seen that the supply of electroactive molecules or ions to the electrode surface can be maintained eitherby some process of mass transport from the bulk of the phase or by a (potential independent) chemical reaction occuring in the electrolytic phase near the interface.
- The principal mechanism of mass transport in batteries are diffusion in a concentation gradient and migration in an electric field

Concentration overvoltage

- If ions are present in the electrolyte which are not involved in the electrode process, then transport by electromigration may be small. On the other hand, when the electroactive phase, it is not possible to distinguish mass transport polarization and ohmic potential drop. For an electrode process Ox + ne$^-$ → Red, concentration overvoltage is given by

$$\eta = E - E_{eq} = \left\{E^0 + \frac{RT}{nF}\ln\frac{[Ox]_0}{[Red]_0}\right\} - \left\{E^0 + \frac{RT}{nF}\ln\frac{[Ox]}{[Red]}\right\}$$
$$= \frac{RT}{nF}\ln\left\{\frac{[Ox]_0}{[Ox]}\frac{[Red]}{[Red]_0}\right\}$$

where $[Ox]_0$ and $[Red]_0$ represent the concentrations of electroactive species adjactent to the electrode surface as the result of passing a particular level of current.

In the case of mass transport by pure diffusion, the concentrations of electroactive species at an electrode surface can often be calculated for simple systems by solving **Fick's equations** with appropriate boundary conditions. A well known example is for the overvoltage at a planar electrode under an imposed constant current and conditions of semi-infinite linear diffusion. The relationships between concentration, distance from the electrode surface, *x*, and time, *t*, are determined by solution of fick's Second Law so that the expressions can be written for $[Ox]_0$ and $[Red]_0$ as functions of time. Thus for

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$$

and assuming (i) that the activity of the deposed metal remains at units, and (ii) that the surface layer is not completely depleted of $M^{n+}_{(aq)}$ ions, then

$$[M^{n+}]_0 = [M^{n+}] - \frac{2it^{1/2}}{nFAD^{1/2}\pi^{1/2}}$$

i is the constant impressed current

D is the diffusion coefficient of $M^{n+}_{(aq)}$

Stationary layer model

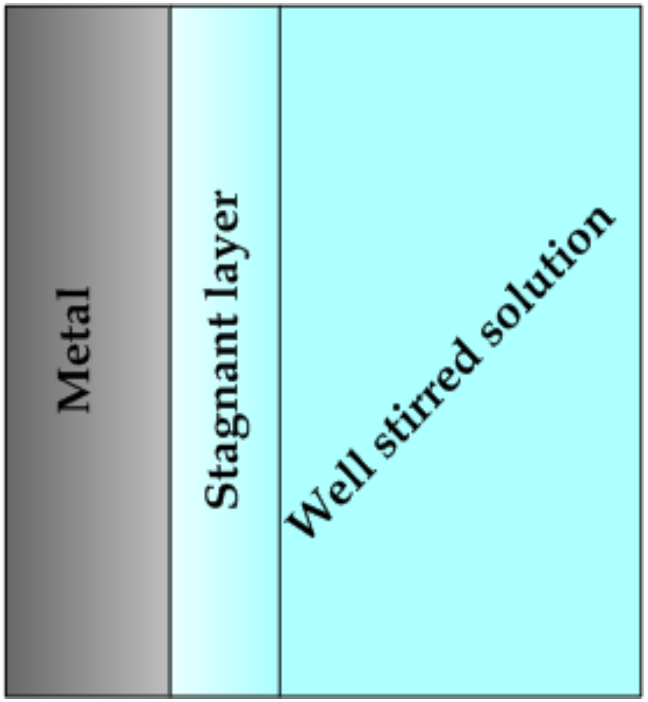
Further,

$$\underbrace{E = E^0 + \frac{RT}{nF}\ln[M^{n+}]_0 \quad \text{and} \quad E_{eq} = E^0 + \frac{RT}{nF}\ln[M^{n+}]}$$

$$\eta = \frac{RT}{nF}\ln\frac{nFAD^{1/2}\pi^{1/2}[M^{n+}] - 2it^{1/2}}{nFAD^{1/2}\pi^{1/2}[M^{n+}]}$$

In most practical situation it is not possible to obtain an analytical expression of this type

This model predicts that after polarization for an initial period, a time-invariant overvoltage will be established.



Stationary layer model

Stationary layer model

- The **Stationary layer model** has been applied with some success to unstirred system where it is thought that natural convection caused by density variations (arising from changes in the composition of electrolyte due to the electrode reaction) permits a similar layer system to be established. Such a model is not applicable where the electrolyte is immobilized, nor is it useful for electrodes with rough or porous surfaces.
- For the process $M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$ and assuming first that diffusion is the only mechanism of transport across the stationary layer, in the steady state, the flux of electroactive species across the layer must be balanced by the flux of charge at the electrode surface. For a linear concentration gradient across a stationary layer of thickness δ, application of Fick's First Law gives:

$$i = nFAD\left\{\frac{[M^{n+}] - [M^{n+}]_0}{\delta}\right\}$$

Stationary layer model

- The form of this equation shows that the concentration gradient can have any value from zero up to a maximum of $[M^{n+}]/\delta$ where the surface concentration of $M^{n+}_{(aq)}$ has fallen to zero. This maximum concentration gradient is associated with a maximum or **limiting** current given by

$$i_{lim} = nFAD\,[M^{n+}]/\delta$$

- Note that it is straightforward to correct equation for electromigration. Thus

$$i = nFAD\left\{\frac{[M^{n+}] - [M^{n+}]_0}{\delta(1 - t_{M^{n+}})}\right\}$$

and

$$i_{lim} = nFAD\left\{\frac{[M^{n+}]}{\delta(1 - t_{M^{n+}})}\right\}$$

trasport number of $M^{n+}_{(aq)}$ in solution

Stationary layer model

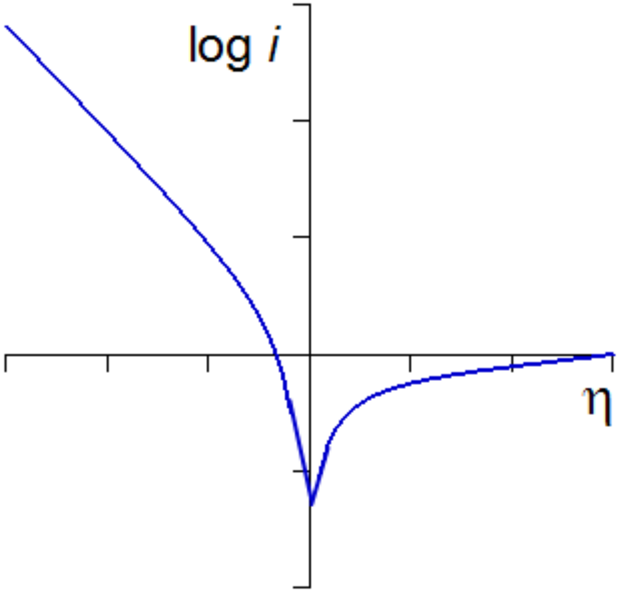
- The diffusion overvoltage according to this model can be evaluated using the relationship

$$[M^{n+}]_0 = (1 - i/i_{lim})[M^{n+}]$$

so that

$$\eta = \frac{RT}{nF} \ln \frac{i_{lim} - i}{i_{lim}}$$

- It should be remembered that in the case of metal/metal ion electrode, the current can only be mass-transport limited in the cathodic direction.
- For net anodic currents, an accumulation of metal ions occurs at the electrode surface.



Current-voltage for a metal-metal ion electrode

- The anodic current can greatly exceed the limiting cathodic current and under these circumstances equation can be simplified to give

$$\eta = \frac{RT}{nF}\ln\frac{|-i|}{i_{lim}}$$

where *i* refers to the anodic current and i_{lim} to the limiting cathodic current. Hence

$$\eta = \left\{\frac{RT}{nF}\ln i_{lim}\right\} - \frac{RT}{nF}\ln i$$

This equation has exactly the same form as the Tafel equation: a linear Tafel plot does not necessarily imply a charge-transfer limited process

- In the models for mass transport considered so far, it has been assumed that the electrode surface was smooth. In practice rough or porous structures are commonly used in battery systems to increase the “real” surface area and so reduce the charge transfer overvoltage.

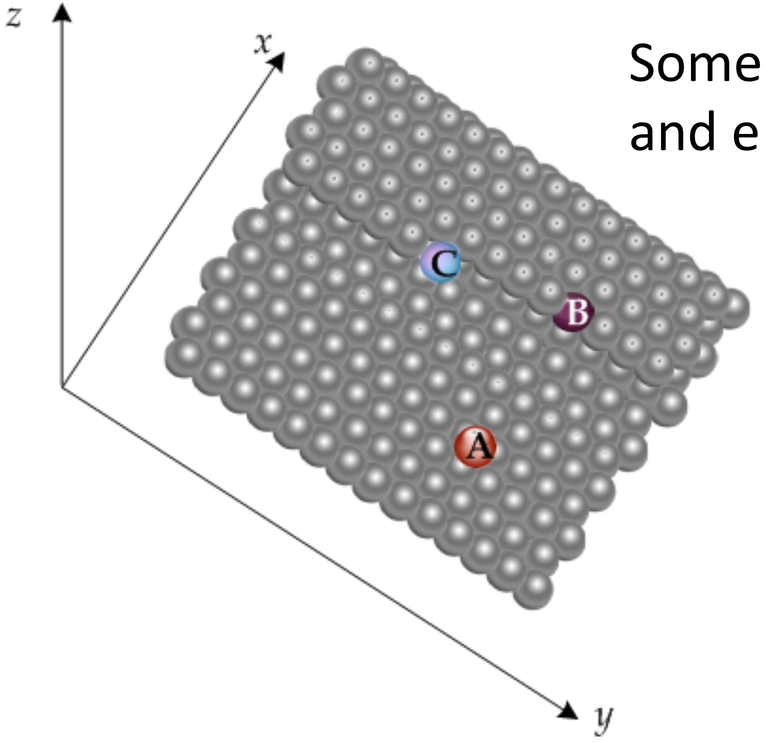
- When surface irregularities are of the same order of magnitude as the thickness of diffusion layer δ, calculation of diffusion flux becomes very difficult. With porous electrodes the real surface area may be $10^4 – 10^5$ times greater than the projected or geometric surface.
- However the presence of pore structure imposes fundamental changes both on charge-transfer kinetics because of the altered potential distribution and on mass-transport control because of the effect of the pores on concentration gradients. A number of simple models have been studied (e.g. a sequence of parallel cylindrical pores), and while there are no general solutions, a number of limiting cases have been described quantitatively.
- In addition to mass transport from the bulk of the electrolyte phase, electroactive material may also be supplied at the electrode surface by homogeneous or heterogeneous chemical reaction

- For example, hydrogen ions required in an electrode process, may be generated by dissociation of a weak acid. Ad this is an uncommon mechanism so far as practical batteries are concerned (but not so for fuel cells) the theory of reaction overvoltage will not be further developed here. However it may be noted that Tafel-like behaviour and the formation of limiting currents are possible in reaction controlled electrode processes.
- The discussion of concentration polarization so far has centred on the depletion of electroactive material on the electrolyte side of the interface. If the metal deposition and dissolution processes involve metastabel active surface atoms, then the rate of formation or disappearance of these may be the critical factor in the overall electrode kinetics.

- Rewritten for "**Crystallization overvoltage**":

$$\eta = \frac{RT}{nF}\ln\frac{\left[M_{(ad)}\right]_{eq}}{\left[M_{(ad)}\right]}$$

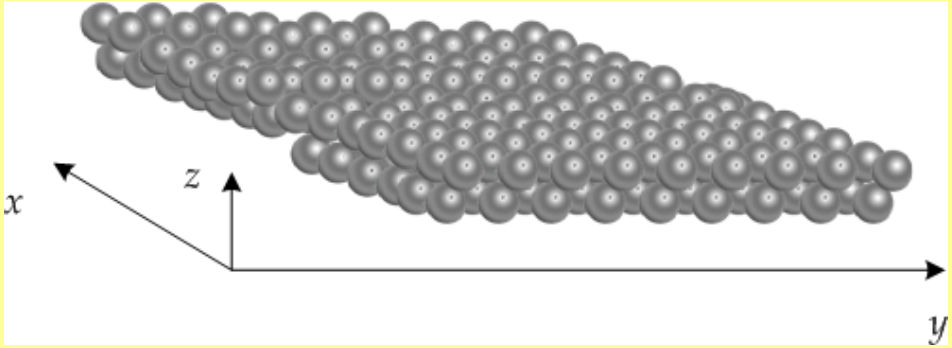
where $[M_{(ad)}]_{eq}$ and $[M_{(ad)}]$ represent the surface concentration (or better, activities) of *M* adatoms on the metal surface under conditions of equilibrium and current flow respectively.



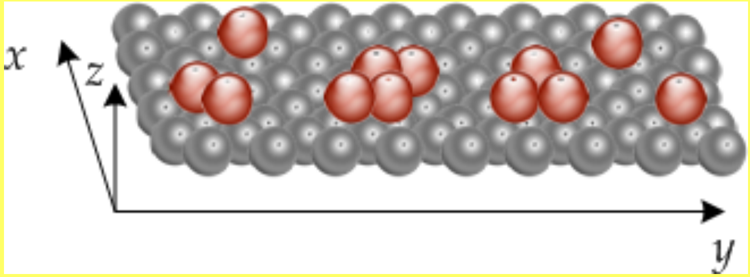
Some features associated with electrocrystallization and electrodissoltion are shown.

Electrocrystallization on a metal surface. Upper layer of atoms grows by surface diffusion of **adatoms (A)** across the plane XY until they encounter **step site** of lower energy, such as **B.** The adatom may now move along the step until it is located at the even lower energy **kink site at C.**

At low current densities, electrocrystallization is thought to proceed by incorporation of adatoms in step sites. The steps may then grow, and provided that each step is located at a screw dislocation. The number of step sites remains constant during deposition or dissolution.



Electrocrystallization on a metal surface. Growth can proceed continuosly in the Z-direction as the step rotates around the screw dislocation



Electrocrystallization on a metal surface. At high concentrations of adatoms two-dimensional surface nuclei may form which provide growth steps.

At higher current densities surface nucleation occurs, thus greatly increasing the number of growth sites.

- At high anodic current densities a different form of surface nucleation must be considered: the formation of cavities, one atom deep. When discussing electrocrystallization or electrodissolution overvoltage, it is assumed that the phase transfer process itself does not restrict the current. The limiting process is the supply or removal of M asatoms on the surface. This in turn may be affected by the rate of surface diffusion, the rate of interaction of adamatos with growt steps, the concentration and distribution of nuclei, etc…
- The overvoltage may therefore follow a wide variety of current functions. If surface diffusion is rate-limitng, then in the simplest cases the overvoltage/current relationship becomes indistinguishable from that of charge transfer.
- This is also the case for sufficiently large rates of surface nucleus formation. Where both nucleation and screw dislocation growth proceed simultaneously, the current/voltage relationship is complex

- It is therefore seen that the equation for the on-load cell voltages during discharges and charges respectively can be expanded to give:

Cell Discarges

$$\begin{aligned} E_{cell} &= E_{thermodynamic} - E_{pol} \\ &= E_{Thermodinamic} - \eta_{cathode} - \eta_{anode} - iR \end{aligned}$$

Cell Undergoing Charge

$$\begin{aligned} E_{cell} &= E_{thermodynamic} + E_{pol}^{'} \\ &= E_{Thermodinamic} + \eta_{cathode}^{'} + \eta_{cathode}^{'} + iR \end{aligned}$$

- The cathodic and anodi overvoltages depend on the dominant rate limiting processes for a particular current density and direction.

Battery characteristics and performance criteria

A cell may be characterize in terms of:

i) Its available capacity
ii) Its available energy
iii) The power it can deliver

It is not very useful to consider efficiency in the sense used to assess heat engines since batteries cannot be regarded aas thermal converters. Rather, the efficiency of an electrochemical power source can be expressed in terms of capacity or of energy delivered.

Capacity

- During the discharge, the battery delivers energy, and the amount of this energy is described as the capacity. The precise definition of capacity is importatn, because it is not an unamiguous quantity, bu depends on the condictions in which it is determined.
- The theoretical capacity of a cell or half-cell may be calculated as:

$$Q_T = x(nF)$$

where *x* is the theoretical number of moles of reaction associated eith the complete discarge of the cell. The **pratical capacity** or actual numeber of coulombs or ampere hours delivered, Q_P, is lower that Q_T if utilization of electroactive material is not 100% due, for istance, to some chemical reacrion occuring in the cell which consumes some of the reactants. The **rate capacity** is the practical capacity of a cell which has fallen to a pre-selected **cut-off voltage.**

- The **Coulombic efficiency** of a cell is defined as Q_P/Q_T. It is often more useful to determine the capacity of each half-cell separately, since for operational reasons, most practical batteries do not have an equal numeber of equivalents of anodic and cathodic reactants.
- For purpose of comparison, it is convenient to calculate the **specific capacity**, defined ad the capacity divided by the mass of the cell or half-cell, and usually given in units of **$Ah\cdot kg^{-1}$**. In some cases a volume-based specific capacity is preferred (e.g. $Ah\cdot dm^{-3}$).

Ah capacity (C_{Ah})

In the general battery practice, it is more usual to measure only the current output, since its more convenient ans sufficient in most cases for comparison. This definition of capacity is

$$C = \int_0^t I(t)\mathrm{d}t$$

To derive the energy output, the so defined “Ah capacity” has to be complemented by indications concerning the voltage. Corresppondіng terms are:

a) Starting discharge voltage or Initial discarge coltage: voltage at the moment the load is applied. For lead-acid batterie, usually defined as the voltage after 10% of the capacity has been discharged, and an initial voltafe anomaly, the ‘coup de fouet’ has been passed

b) End-of-discharge voltage or final voltage: voltage that determines the end of the discharge. It is defined by the battary manufacturer, to specify the discharge performance of the battery. But it may also be specified by the battery user according to the requirements of the application. Any comparson of capacity data must always consider the end-of-discharge voltage

- Average discharge voltage or mean discharge voltage: approximate average of the voltge during the whole discharge period

$$average\ discharge\ voltage\ \times current = discharge\ energy$$

- Mid point discharge voltage: voltage after 50% of the capaicity has been discharged (≈ average voltage)
- When the battery is discharged with a constant current, which is mainly done in the laboratory the equation of capacity is simplified to

$$C = I \cdot \Delta t$$

- *F*: Faraday 96485 C/equiv
- ***1·F = 96485 (C /equiv)· (1h / 3600s) = 26.802 Ah/equiv***
- ***2·F = 53.604 Ah/equiv***

Relationships $C_{Ah} \Leftrightarrow$ weight, volume

- The relationship between current and amount of water decomposentd or the equivalent volumes of gas generated can be evaluated from

$$H_2O \Longrightarrow H_2\uparrow + \frac{1}{2}O_2\uparrow$$

  Using the Faraday const

- The number of exhange electrons is 2

$$\enclose{circle}{P} = \frac{i(\mathrm{Ah})}{nF\left(\frac{\mathrm{C}}{\mathrm{eq}}\right)} \cdot 3600(\mathrm{s}) \cdot \enclose{circle}{PM}$$

Peso in grammi

Molecular weight

- 1Ah decomposes 0.3361gH_2O and generates 0.0376gH_2 + 0.2985gO_2
- 1 g H_2O is the equivalent of 2.975 Ah

$$\begin{cases} 3Ah <\simeq> 1g\ H_2O \\ 1Ah <\simeq> 1/3\ g\ H_2O \end{cases}$$

Nominal or rated capacity

- This capacity is the amount if charge that is expected to be delivered from a fully-changed cell or battery for a specified discharge rate, temperature and discharge cut-off voltage
- It has become accepted practice to normalize the current (ampers) during discharge to the rated capacity and the express the discharge rate as

$$\boxed{C_x/_t} \qquad \boxed{C = I_d \cdot t_d^*}$$

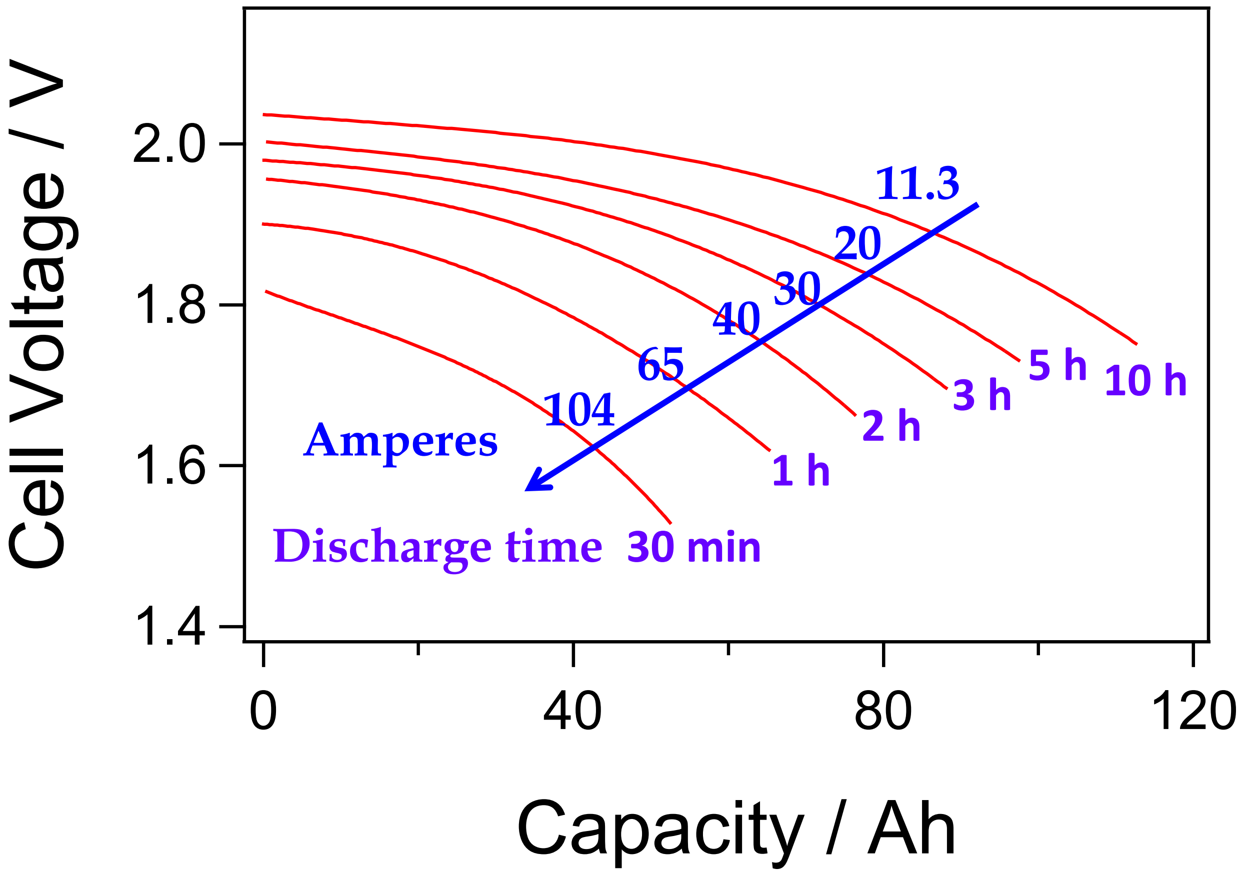
x = hour rate for the rated capacity

t = a time specification in hours

Example:

A battery with a nominal capacity of 175 Ah at the $C_5/5$ rate at 25°C would supplu 35A

Typical discharge characteristics



Typical discharge characteristics of lead/acid EV batteries, base: 100 Ah at C5/5 rate

Example

a) A battery specified to have a 100 Ah capacity at the 5h rate deliver a constant current of 20A for 5 h at the given temperature, thus, this battery has a nominal capacity of 100Ah at the $C_5/5$ rate.

b) By way of es., taking a current of 50A from this battery can be expressed as discharge at the $C_5/2$ rate.

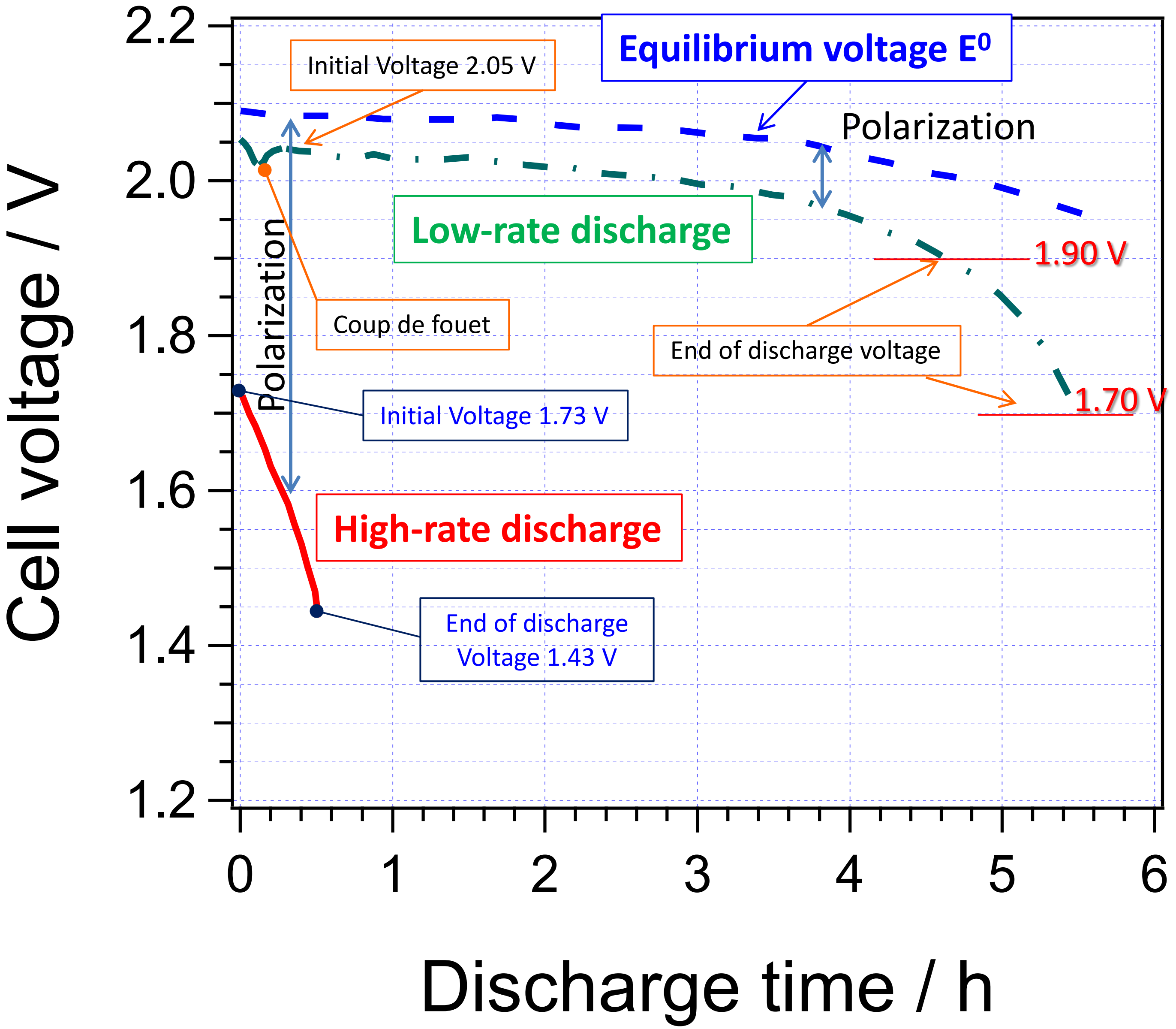
- This is simply an expression of the current used and does not simply that the battery can be discharged at this same current for 2 h ($C_2/2$ 40A)
- Rated capacities of starter batteries (SLI) and small portable batteries usually are referred to the 20h discharge rate
- Th rated capacity of conventiona stationary lead-acid batteries is based on the 10h discharge in Europe and on 8h discharge rate in the US.

- The rated capacities of traction batteries mostly are related to the 5h discharge rate, and this applies also to many of the alkaline batteries
- 10h discharges are also used to specify the rated capacity of nickel/cadmium batteries
- Note: the nominal or standard capacity is an important parameter that characterises the enery content of the battery. Comparison of rated capcities can, however, be misleading when the batteries are selected for discharge condictions that are considerably different from those that specify the rated capacity. Then the influence of the various discharge parameters must be conseidered, and the comparison of capacities under such condictions can have a quite different result

Retained capacity

- The high-rate discharge is to a large extent determined by rather slow diffusion processes. After an interruption period, required for equalization, the discharge rate can be continurd at a lower rate or, to a limited extent at the high rate. The charge removed from the battery durin the second step is called the retained capacity. In the sequence high-rate/low-rate discharge, the sum (high-rate capacity + retained capacity) equals approximately the normal low rate capacity of the battery.
- The capacity that can be drawn from a battery under a certain load depends on the rates of reaction that determine the discharge characteristic. For this reason, it depend on the kinetic parameters that influence the rates of the barious reaction steps, as ahs been described. Thus, the capacity depends to a large extent on the design of the battery, there is a wide variation of such design parameters like plate thickness, plate distance, specific plate surface and similar parameters.

Discharge parameters



Discharge parameters

The discharge parameters, beside the design of a battery, that mainly influeced the capacity are:

- ✓ **discharge current**
- ✓ **voltage limit**, i.e. the final voltage or end-o-discharge voltage, that has to be specified ad described below
- ✓ and **temperature**

Further parameters that also influence the capacity are the state of charge and, to some extent, the previous history of the battery.

At high discharge rates, the cell voltage is so far reduced that the end-of-discharge voltage, used for the low-rate discharge, would limit the discharge at very biginning. As a consequence, in battery practice the end-of-discharge voltage is often reduced with incresing load. The end-of-discharge voltage is reduced step-by-step from 1.85 V/cell to 1.675 V/cell for discharge rates between 10h and 0.25h. But this is not practized uniformly. In the US for example, it is more general use to specify 1.75V/cell as end-of.discharge voltage for a wide range of loads and only reduce this value for extremely high loads.

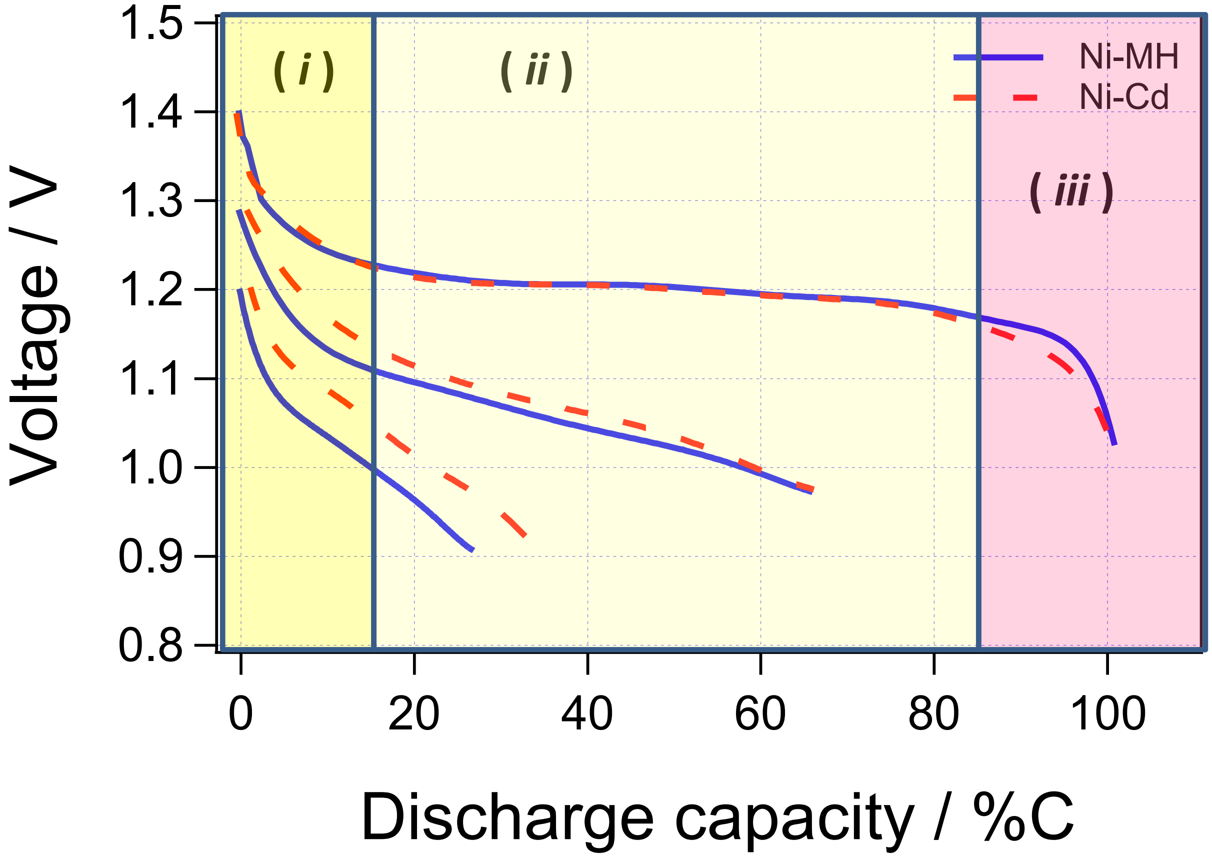
Discharge parameters

The coup de fouet or initial voltage minimum (in German “Spannungssack = voltage pocked”) is a voltage minimum at the beginning discharge of fully charged lead-acid batteries in the range of 20 mV/cell. It is caused by the positive electrode, and can be ascribed to crystallization overvoltage. (*Ni/Cd and Ni/Metal hybride batteries do not show a corresponding effect*)

The coup de fouet is observed at low and medium discharge rates

Ni/Cd and Ni/MeH batteries show similar discharge behviour. Only at high loads, the capacity reduction of Ni/metal hydride battery is slightly higher since desorption rate of hydrogen becomes limiting (C_5 is of course higher for the Ni/metal hydride battery)

Ni/Cd, Ni/MH batteries

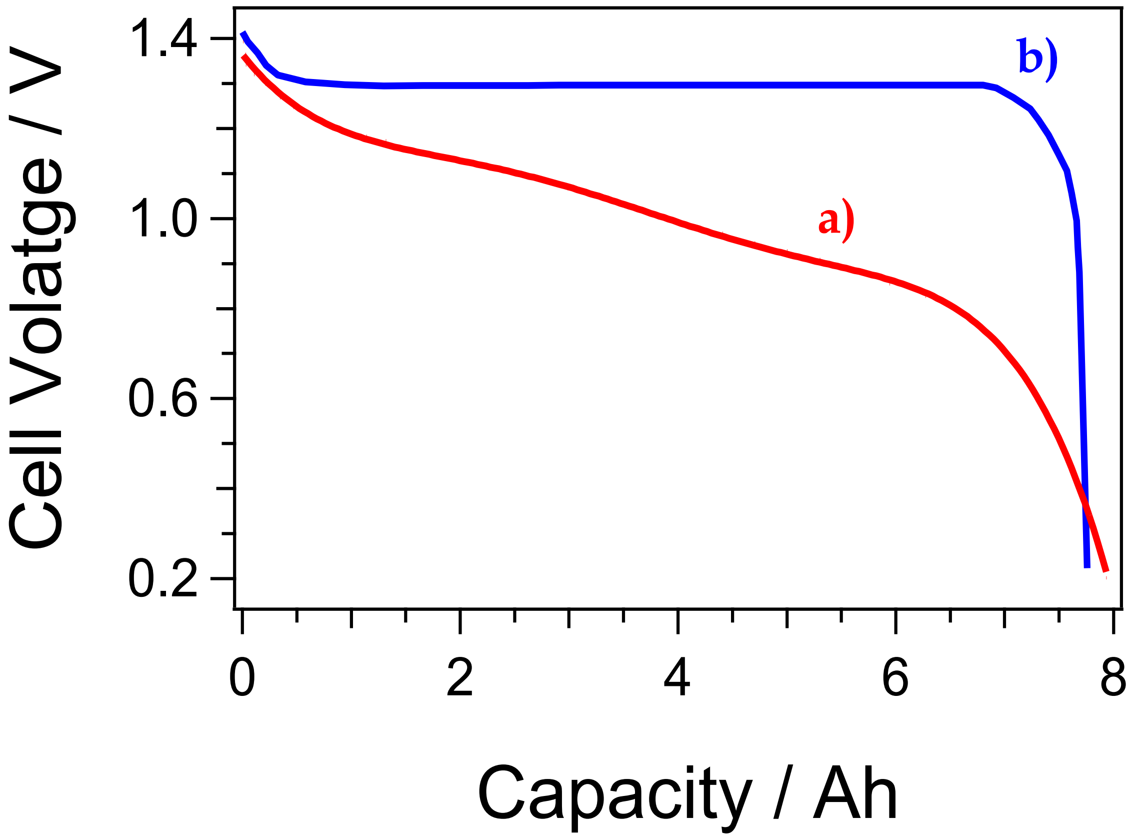


Discharge curve for button cells (Ni/Cd and Ni/MH). Voltage referred to percentage of the rate capacity (C_5). Current ratings in multiples of the rated capacity

(i) Electrode polarization overvoltage (associated to a large extend with one of the two electrode processes;

(ii) *iR* polarization

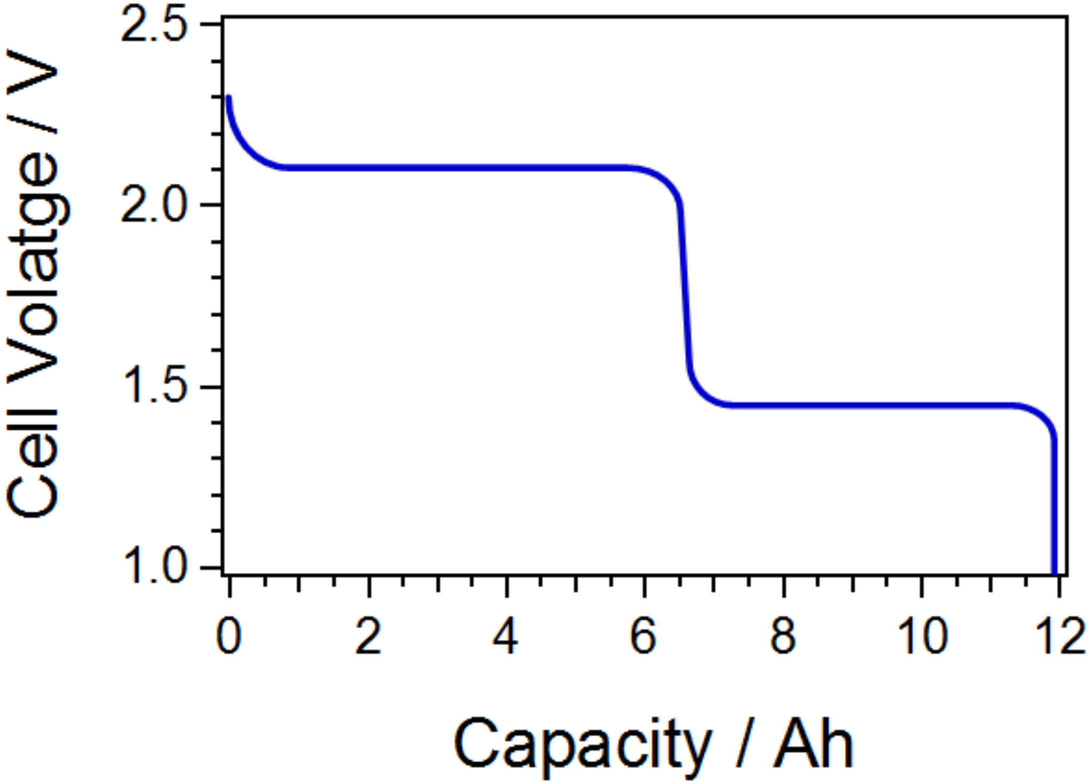
(iii) *iR* + depletion of electroactive materials



Discharge curves for typical cathodic half-cells

a) Reactants and products in solution phase, e.g. $Fe^{3+}_{(aq)}$ and $F^{2+}_{(aq)}$

b) Reactants and products both form in solid phase, e.g. $Ag_2O_{(s)}$ and $Ag_{(s)}$

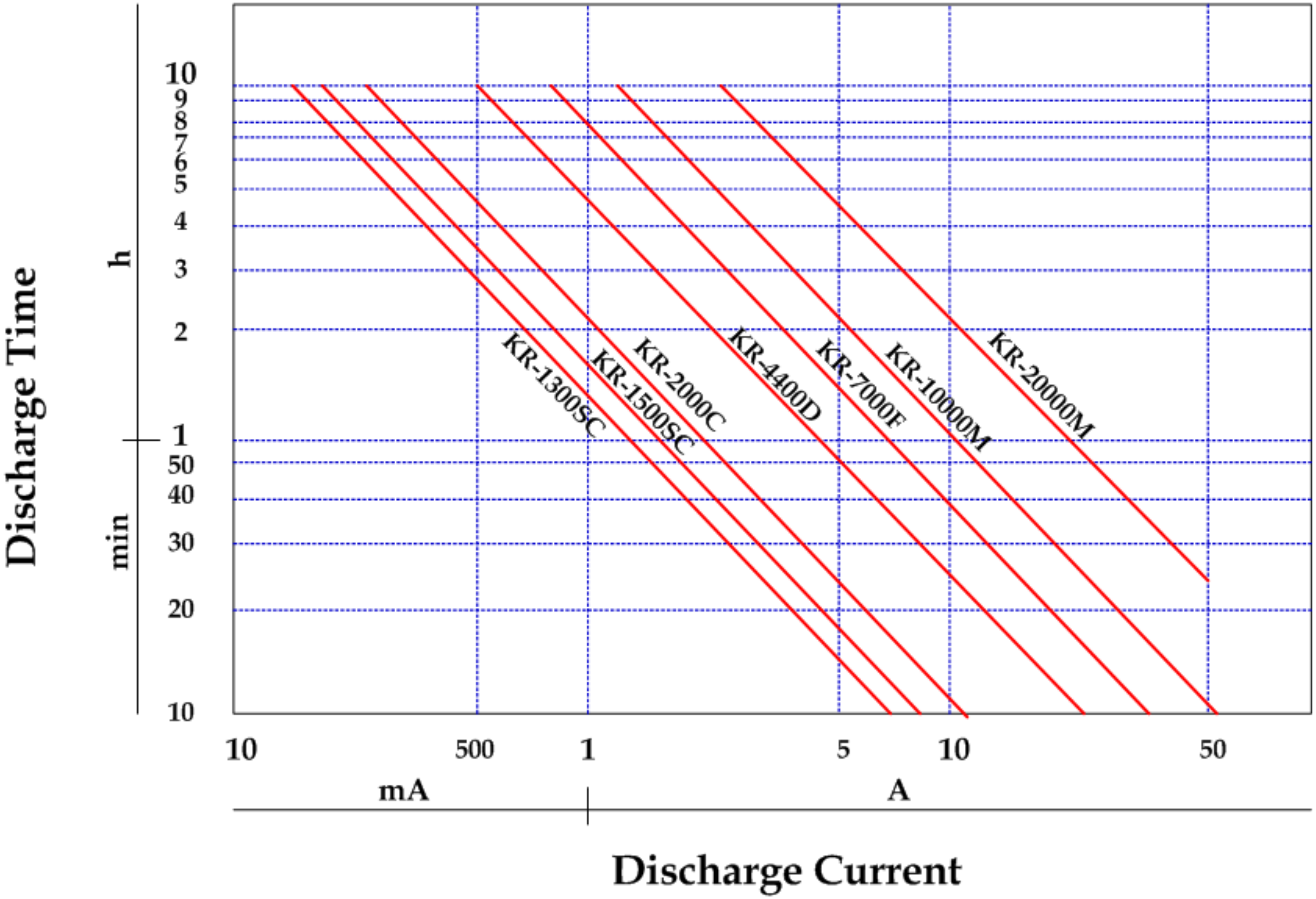


Two stage discharge curve where all three electroactive components form

a) Reactants and products are both in liquid or solid solution
b) Represent the case where they form two distinct solid phases a two-stage discharge takes place, where all three electroactive components form separate solid phases and the electrolytic phase remains virtually invariant, e.g.

$$2CuS_{(s)} + 2e^- \rightarrow Cu_2S_{(s)} + S^{2-}_{(s)}$$

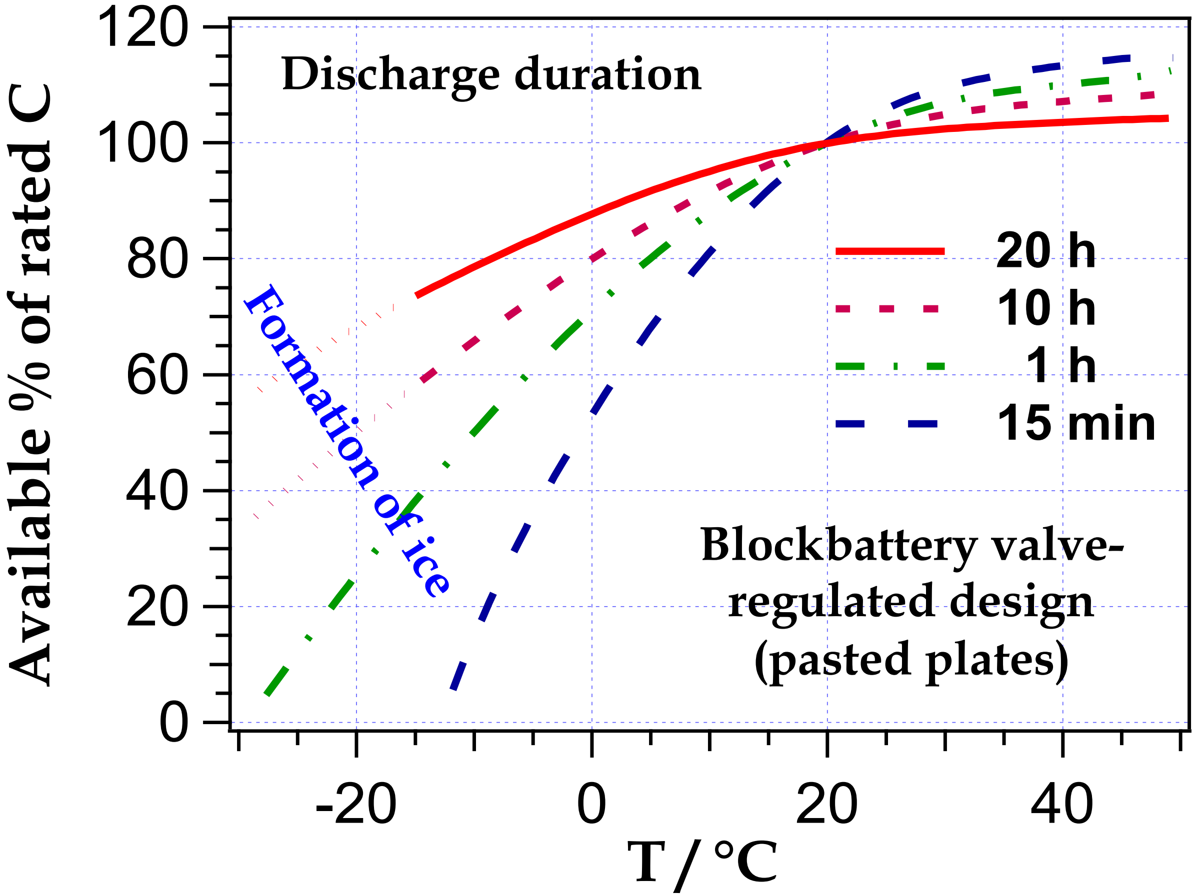
$$Cu_2S_{(s)} + 2e^- \rightarrow 2Cu_{(s)} + S^{2-}_{(s)}$$



Discharge curves for cylindrical sealed Ni/Cd batteries. Discharge time versus discharge current in double logarithmis scles (SANYO)

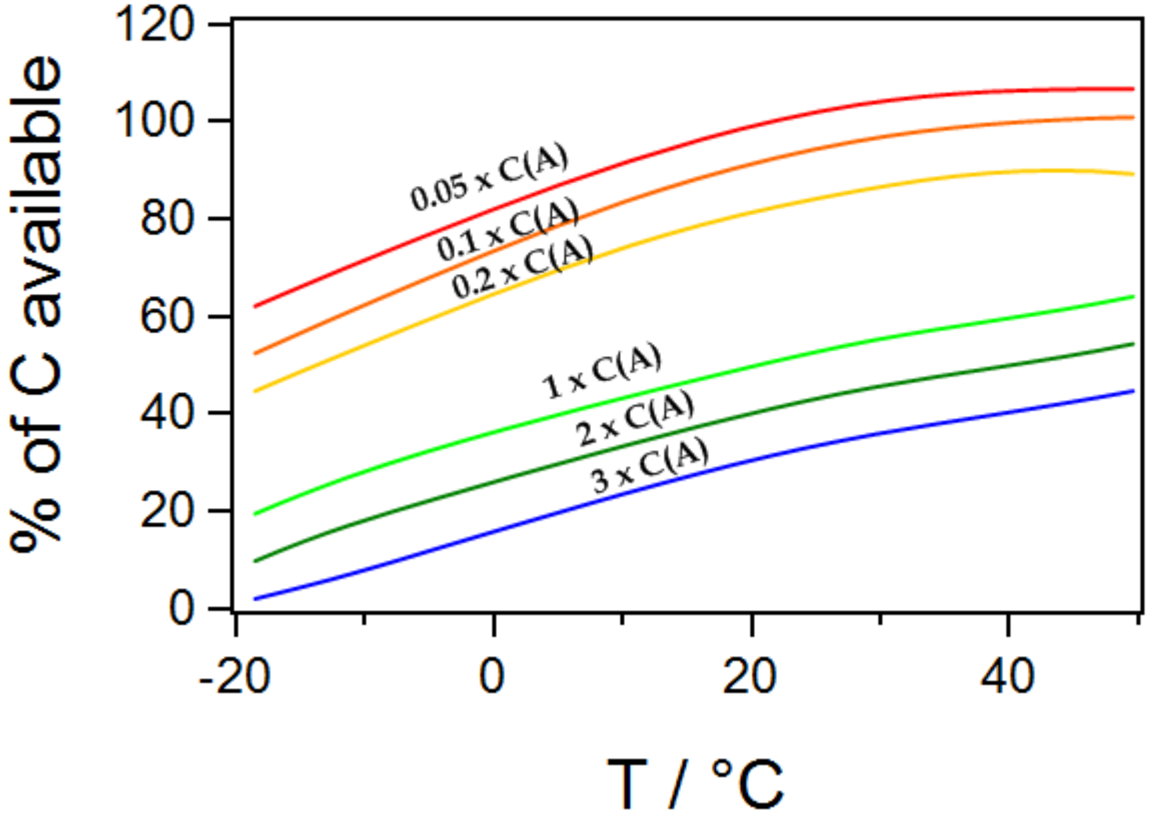
Here discharge duration is plotted versus the discharge current in a double logarthmic scale. The resulting lines allow an easy selection of the appropriate battery size when load and discharge duration are specified.

Temperature Influence on Capacity



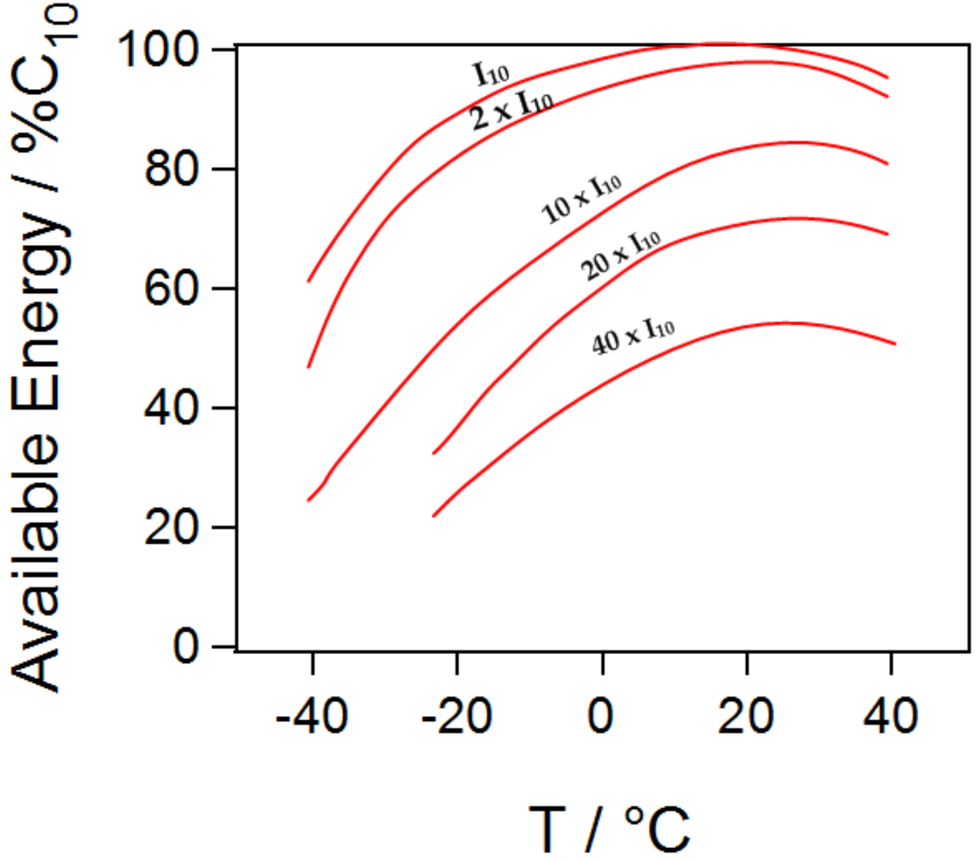
Valve-regulated lead-acid battery. Temperature influence on capacity at various discharge rate (VARTA)

The reason is that hidrance of the kinetics gains more importance at high loads. At T > 20°C, a stronger increase of the capacities at the higher discharge rates is observed, compared to their rated values, since now the kinetic hindranceis reduced and a larger part of capacity is available, that at T_{amb} remains unusued.



Valve-regulated lead-acid battery. Effect of the T and discharge current on C. Curves referred to the 20-h discharge capacity. Yuasa NP series (the current I = 0.05C discharge 100%)

In Ni/Cd batteries, the capacity also is remarkly reduced with decreasing T. although the electrolyte is not diluited, its conductivity is reduced significantly at low T and the kinetics parameters of the reactions also depend on T.

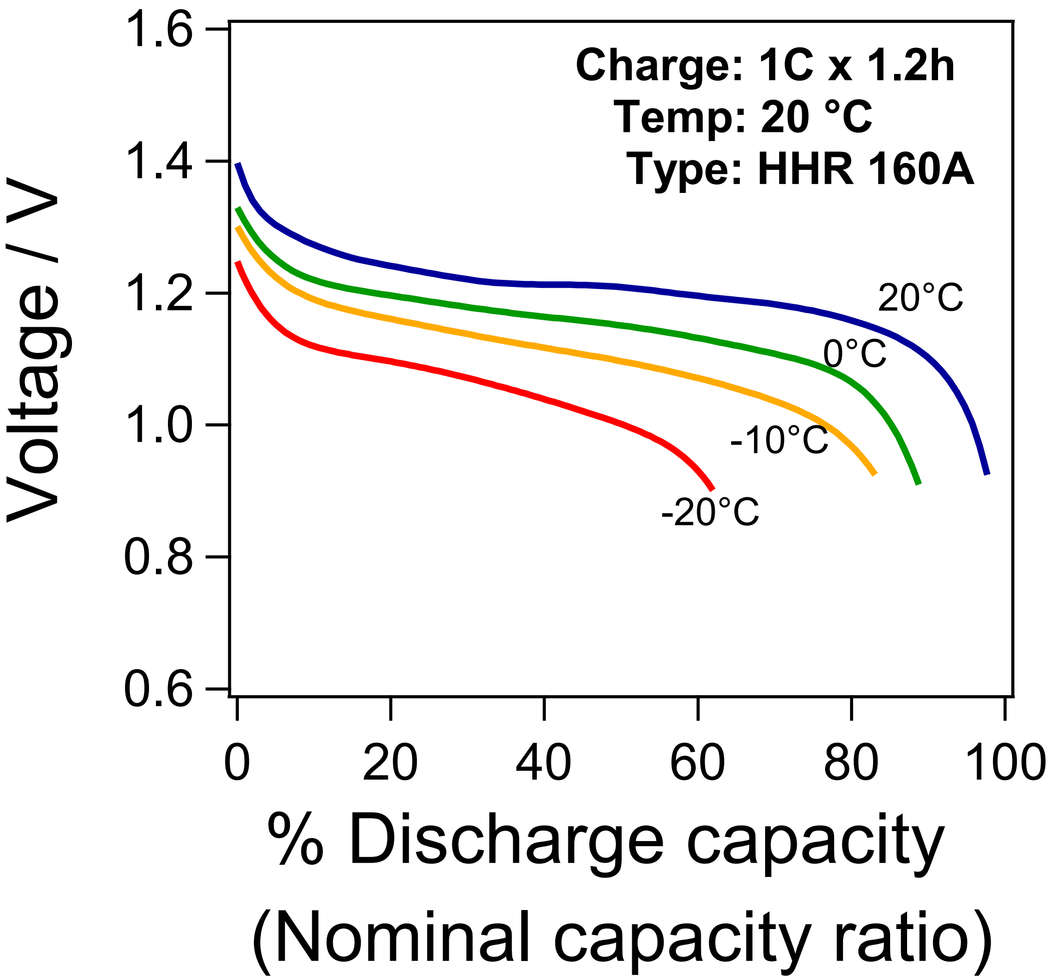


Sealed Ni/Cd batteries. Available energy in % C10 of cylindrical sintered cells as a function of temperature. Charging at the nominal rate at T_{amb} (VARTA RS Type)

The available Capacity rapidly falls with temperature. Since the electrolyte is not diluted during discharge, ice formation is not revelant for Ni/Cd batteries

A decrease of capacity can also be observed at T > 30°C. This is caused by the instability of the higher Nichel hydorxide at elevated temperature

Nichel/Metal Hydride batteries

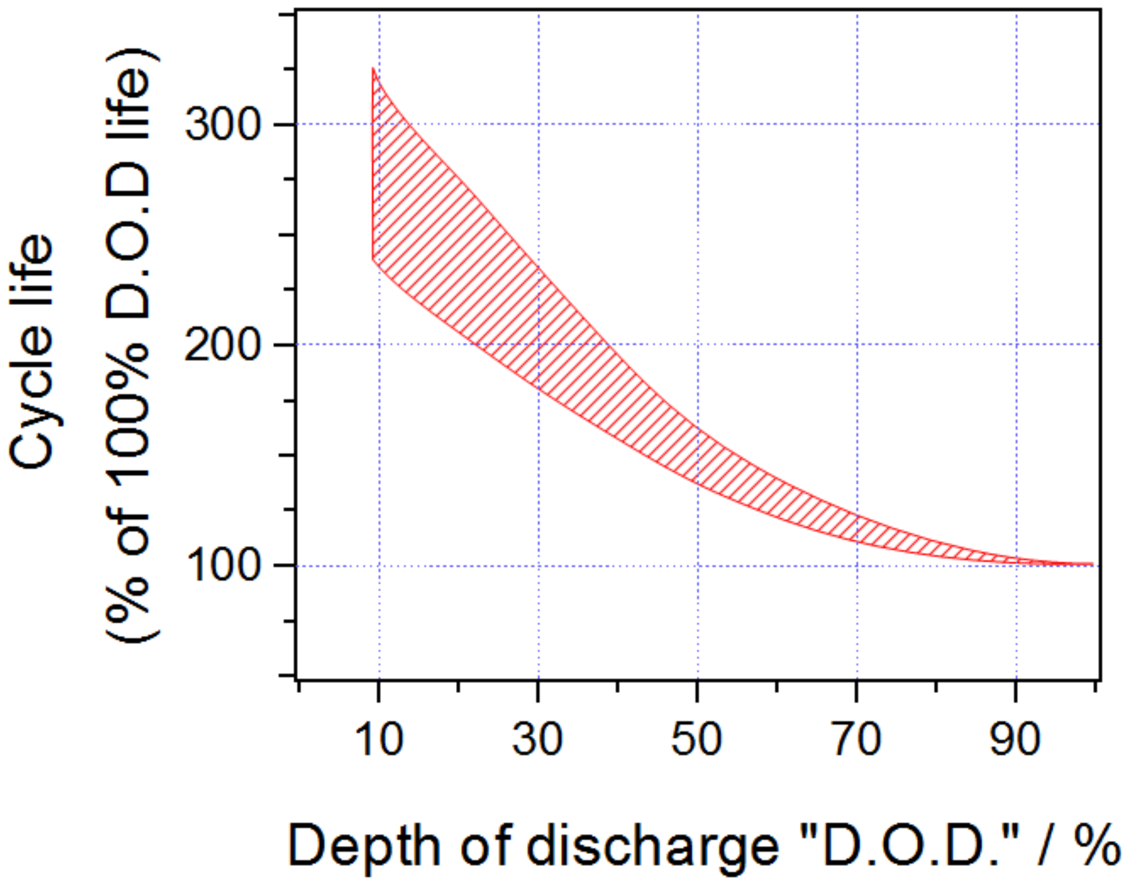


The effect of the T on C is similar to the corresponding effect on Ni/Cd batteries

Nichel/metal hydride batteries. Discharge curves at various T. Discharge at $1C_5$ (Panasonic)

Deep Discharge

- "**Deep discharge**" means that the battery is discharged beyond the end-of-discharge voltage specified by the manufacturer. Thus, an excessive capacity is drawn from the battery.

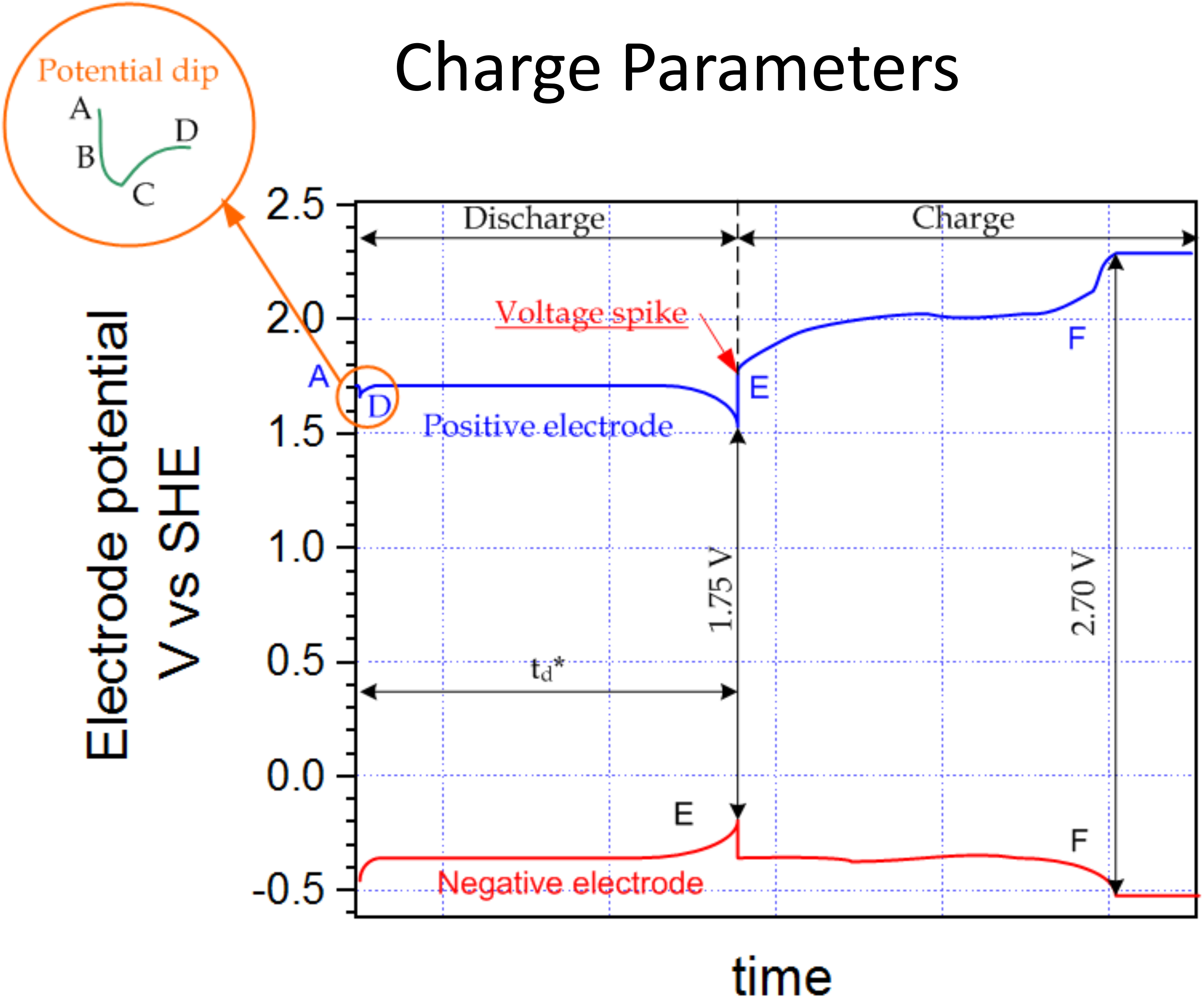


Sealed Ni/Cd batteries. Effect of depth of discharge on cycle life

Deep Discharge

- When the discharge is extended beyond its normal end, the increased stress of the active material can dramatically reduce the number of cycles or cause premature failure.
- Deep discharge is mainly a problem of lead-acid batteries. For Ni/Cd and Ni/Methal hydride batteries, occasional deep discharging are not critical. Prolonged reversal may cause short-circuits in Ni/Cd batteries, because of cadmium dendrites which then grow at the positive electrode, and in Ni/MeH batteries oxidation of the additives such as cobalt oxide can be reduced in the positive electrodes at too low an electrode potential

Charge Parameters



Schematic of discharge – charge characteristics of the lead/acid cell

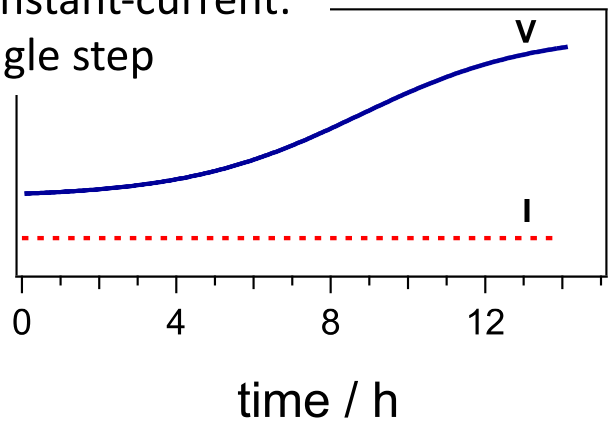
Charge Parameters

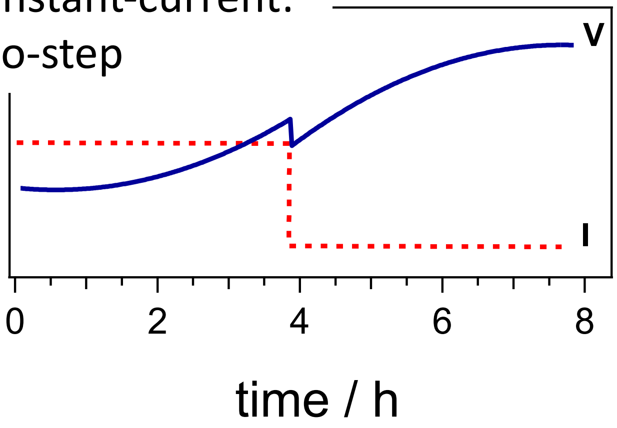
The charging process basically represents the reversal of the discharge. It starts as soon as the voltage of the cell attains a value just above the equilibrium voltage E0. in practice, however, higher voltages have to be applied to achieve a full charge within a desired period and for all cells in the series connecion of a battery. But with incresead cell voltage, the secondary reactions of water decomposition gain more significanceas parasitic reactions. Charging methods therefore always have to compromise between charging at a rather low eate witj high efficiency, and faster but less effective charging. As a consequence, a great number of different charging methods have been developed, adapted to the type of battery as well as to the requirements of the application.

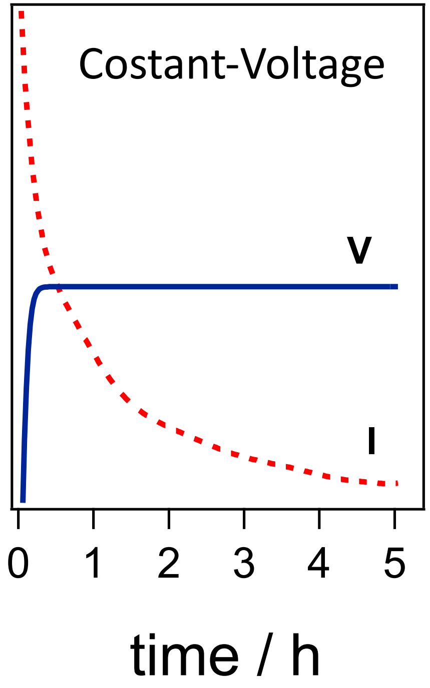
The charging process is mainly influenced by the three parameters:

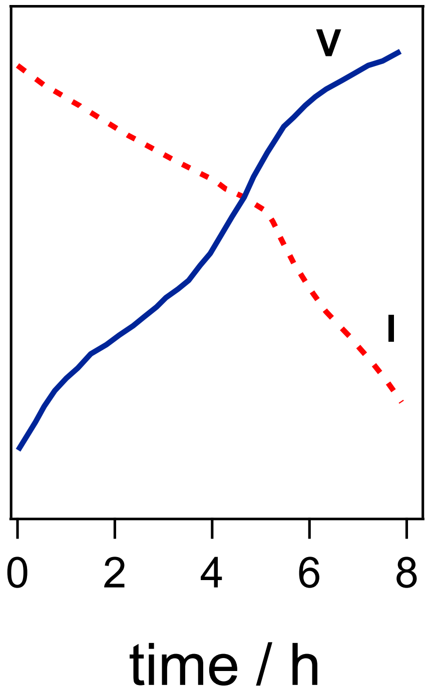
- Charging current;
- Charging voltage;
- Temperature of the battery

Charging procedures and cell characterstics for lead/acid batteries


Constant-current:
single step

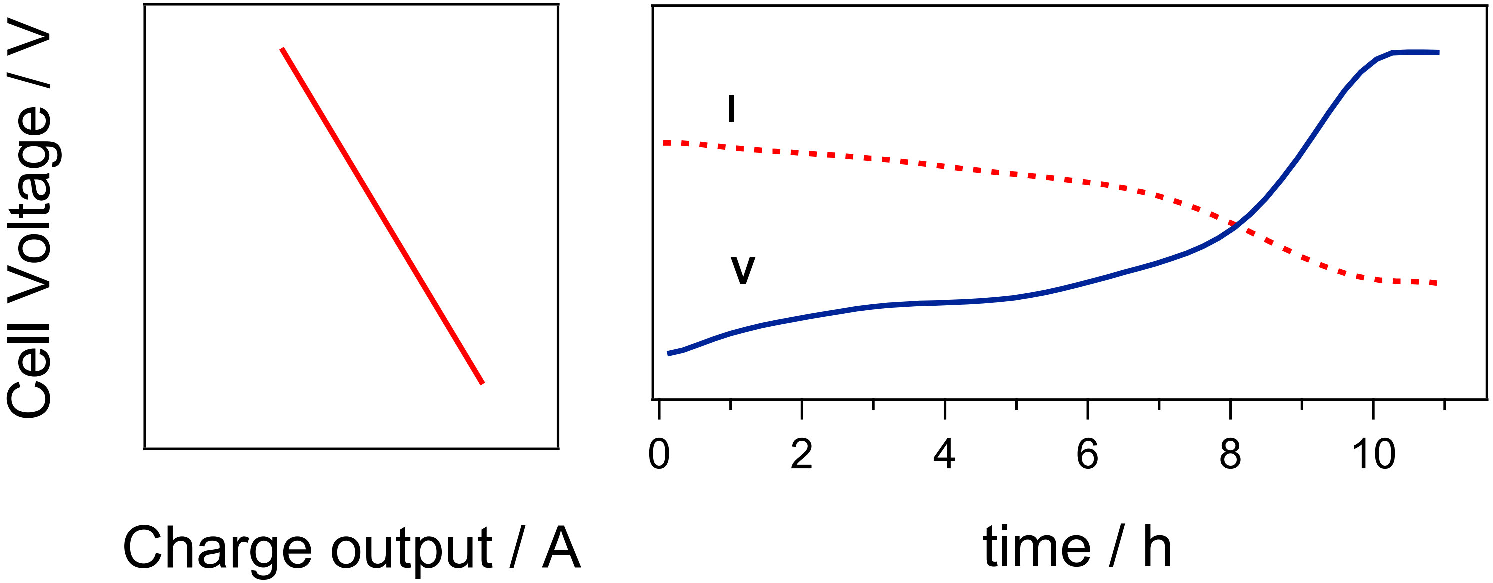

Constant-current:
two-step


Costant-Voltage

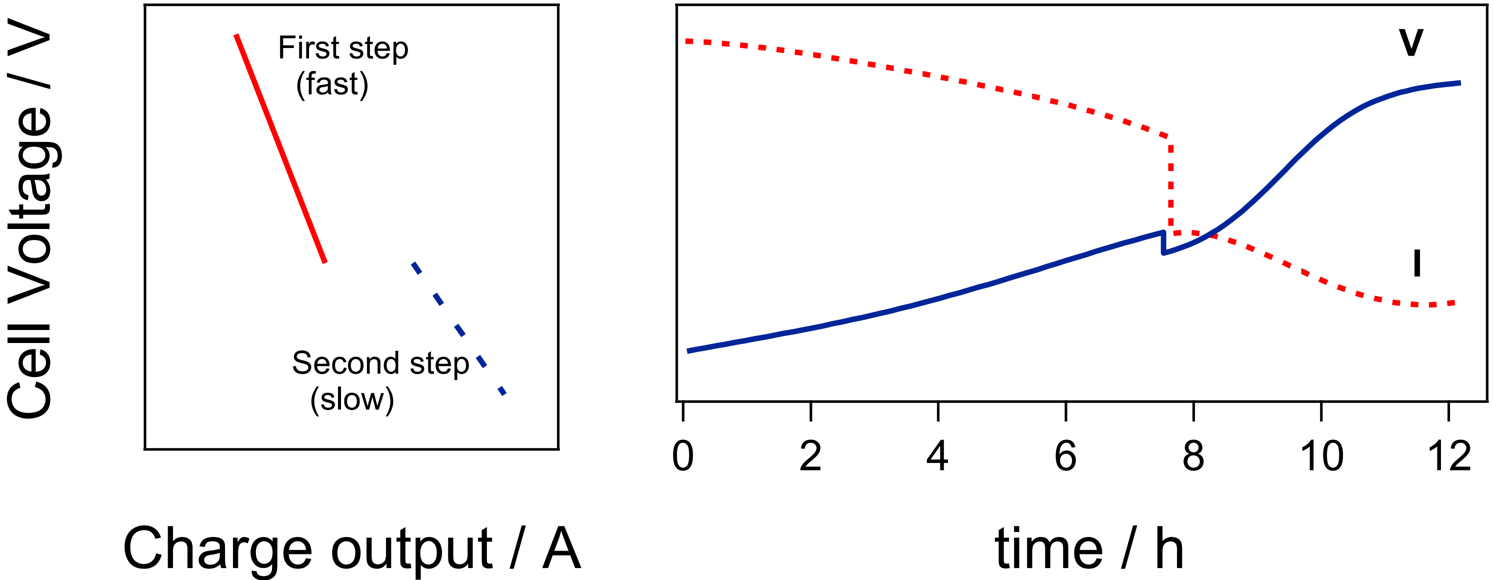

Modified constant-voltage

I = current
V = voltage

Charging procedures and cell characterstics for lead/acid batteries



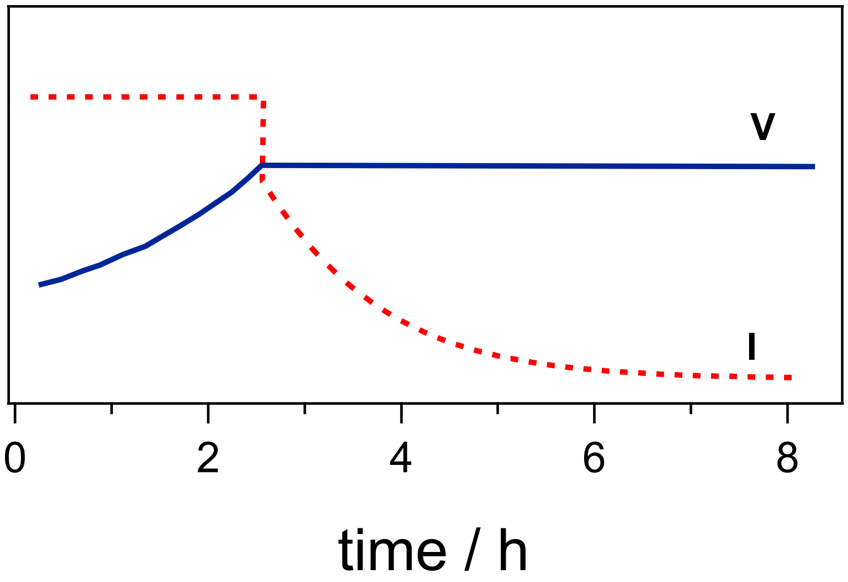
Taper current:
Single-step



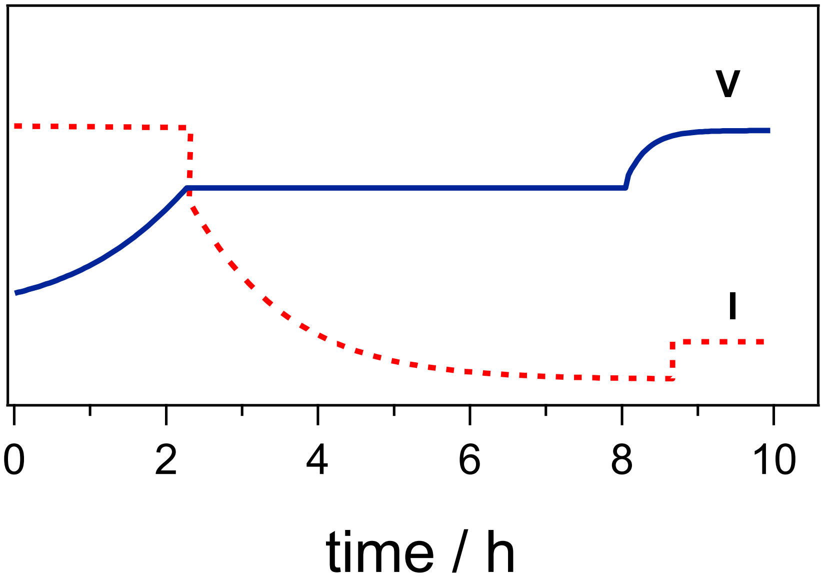
Taper current:
Two-step

I = cell Current,
V = Cell Voltage

Charging procedures and cell characterstics for lead/acid batteries



Constant – Current – Constant – Voltage



Preferred method for VRLA batteries

I = cell Current,
V = Cell Voltage

Energy

The **theoretical available energy** (*ε_T*) for one mole of reaction (not for complete discharge) is given by

$$\varepsilon_T = -\Delta G = nFE_{cell}$$

where E_{cell} is the e.m.f.. The actual amount of energy delivered for one mole of reaction, or **practical available energy** (*ε_P*) is

$$\varepsilon_P = \int_0^{nF} E \cdot \mathrm{d}q = \int_0^{t} (Ei)\mathrm{d}t$$

and id dependent on the manner in which cell is discharged. The units of energy are either joules (i.e. watt seconds) or more commonly Wh (1Wh = 3600 J). The total energy of a cell is sometimes rather confusingly termed the "watt hour capacity". As discussed above, the cell voltage, *E*, deviate progressively from its (maximum) thermodynamic value as the rate of discharge increases. Hence, the **energetic efficiency** $\varepsilon_P/\varepsilon_T$ is a variable quantity, which must be associated with closely defined discharge conditions if it is to be meaningful.

Energy

Theoretical and practical energies can be also expressed in terms of the complete discharge of a particular cell:

$$\varepsilon_T^{'} = x(nFE_{cell}) \qquad \text{and} \qquad \varepsilon_P^{'} = \int_0^{xnF} E \cdot \mathrm{d}q$$

where *x* is again the number of moles of reaction associated with the complete discharge.

The **energy density** (also known as **specific energy**) is the parameter used when assessing relative cell performance. Thus a small battery, weighting, 25 g, and capable of delivering 40 kJ or 0.012 kWh at a particular discharge current, would be said to have an energy density of 480 Wh·kg^{-1}. Again it is sometimes more useful to consider a vlume based specific energy (e.g. Wh·dm^{-3}).

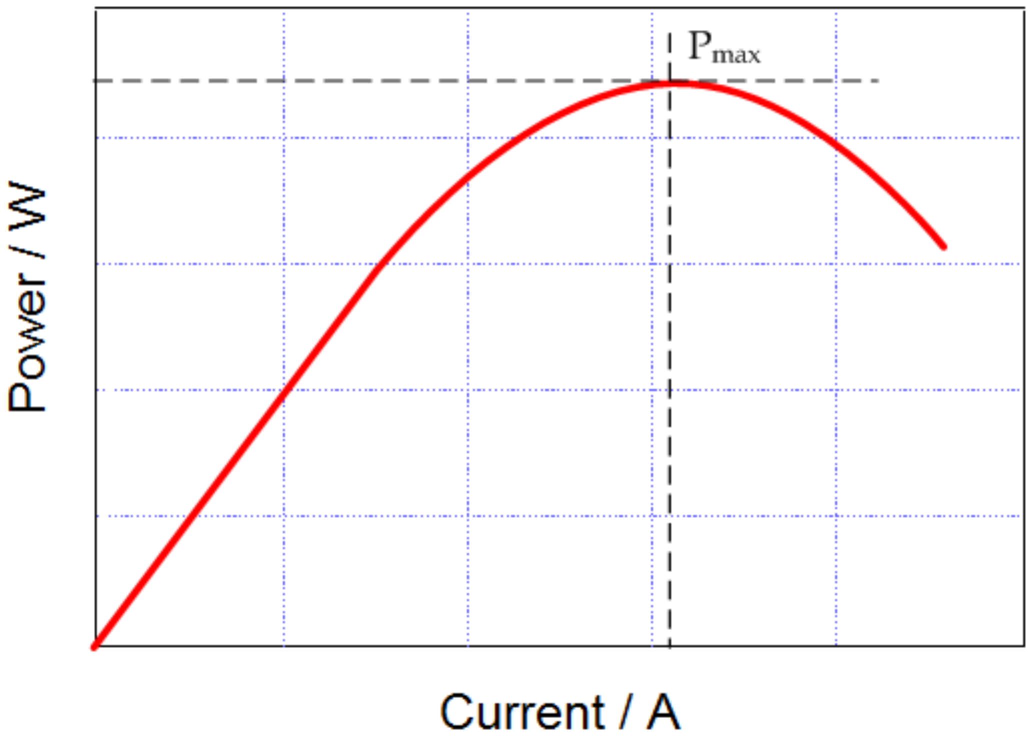
Power

The level of discharge current drawn from a cell is determined principally by the external load resistance. The power deliverd, *P*, is given by the product of the current flowing and the associated cell voltage:

$$P = iE = Ri^2$$

The power rating of a battery specifies whether or not it is capable of sustaining a large current drain without undue polarization. As more and more current is drawn from a cell, the power initially rises; it reaches a maximum and then drops as the cell voltage falls away due to polarization effects. The maximum power point is best determined experimentally by measuring *E* as a function of *i*. In certain circumstances it is possible to calculate the maximum power point – e.g. if electrode polarization is small and the internal resistance of the cell is known. The **rated power** of a battery is the power delivered (in watts) under stated discharge conditions.

Power



The power of a typical electrochemical cell as a function of discharge current

The **rate power density** (or **specific rated power**, W·kg^{-1} or W·dm^{-3}) is again the most convenient parameter for comparing different battery systems

The rated power density and rated energy density are both critical factors when assessing batteries for applications such as motor traction where the battery itself has to be transported. A cell generally has a **maximum permitted continuous power level:** prolonged discharge above this value is liable to cause overheating and a consequent degradation of the cell, as discussed below.

On the other hand, cells may be capable of a much higher **rated instantaneous power level:** prolonged discharge above this value is liable to cause overheating and a consequent degradation of the cell, as discoussed below. On the other hand, cells may be capable of a much higher **rated instantaneous power**. For short discharges the battery does not reach a thermal stationary state and its thaermal capacity my be able to accomodate the heat generated if the thermal conductivities of its constituents are sufficiently high. Furtherm mass transport polarization effects are of less significance for short discharges. Certain batteries, such as those used for starting large diesel engines, depend specifically on their high instantaneous power capabilities.

As will be seen later, cells employing the same chemical system can be designed either for high power or high capacity.

Efficiency of the charging process

On the account of the secondary reactions, the charging process never reaches 100% efficiency. The efficiency actually achieved, depends on the above described parameters. Often the **charging time** is an important parameter for the decision as to which charging method is used to reach both complete recharge and a satisfactory efficiency. This efficiency is expressed either by the

$$\text{Ampere}-\text{hour efficiency}\,\eta_{Ah}=\frac{Available\ capacity\ in\ Ah}{required\ charge\ input\ in\ Ah}$$

$$\frac{\int_0^t i_{dis}\,\mathrm{d}t}{\int_0^t i_{ch}\,\mathrm{d}t}$$

Or its reciprocal, the

$$\text{Ah charging factor}\,\alpha_{Ah}=\frac{Required\ charge\ input\ in\ Ah}{Available\ capacity\ in\ Ah}$$

The overall **cycle energy efficiency.**

For many applications the energy delivered by the battery is the more important parameter. The corresponding relations are

$$\text{Watt} - \text{hour ecciciency}\ \eta_{Wh} = \frac{Available\ energy\ in\ Wh}{Required\ input\ in\ Wh}$$

$$\frac{\int_0^t E_{dis}\, i_{dis}\, \mathrm{d}t}{\int_0^t E_{ch}\, i_{ch}\, \mathrm{d}t}$$

where E_{dis} and E_{ch} are the cell voltages during discharge and charge respectively. Or its reciprocal

$$\text{Watt} - \text{hour charging factor}\ \eta_{Wh} = \frac{Required\ input\ in\ Wh}{Available\ energy\ in\ Wh}$$

On account of the voltage drop between charging and sixcharging, the watt-hour efficiency is always smaller, and the watt-hour charging factor larer, than the corresponding terms reffered to Ah.

Ah and Wh charging efficiencies (η_{Ah} and η_{Wh} respectively) and the Ah and Wh charging factors (α_{Ah} and α_{Wh} respectively) achieved in favorable conditions. These value usually refer to the complete discharge at its nominal rate and a suitable charging schedule that achieves minimum overcharge but ensures complete recharge

Battery system	η_{Ah}	α_{Ah}	η_{Wh}	α_{Wh}
Valve-regulated lead-acid	0.8 – 0.94	1.07 – 1.2	0.65 – 8	1.2 – 1.5
Sealed Ni/Cd and Ni/MH	0.7 – 0.85	1.2 – 1.4	0.6 – 0.75	1.4 – 1.65

Cycle life is the number of times a cell can undergo a charge/discharge sequence before its performance (as measured by its capacity or energy storage efficiency) has been degraded to below some arbitrary limit. For shallow discharge (say<20%) a much longer cycle life is obtained. Standard tests generally required a discharge to 75% or 80% of rated capacity.

Charge retention is a measure of whether the percentage of nominal capacity lost as a function of time due to self-discharge reactions occurring within the cell is lager or smaller. Charge retention is much poorer at high temperatures.

Note 1: Charging efficiency and charging factor are appropriate parameters only for charging processes limited in time. They lose any meaning with prolonged overcharging, e.g. during float charging, when only the secondary reactions are maintained by the current and ‘charging’ no longer occurs. The charging factor would been exceed all limits and the efficiency approach zero.

Note 2: All four parameters in the early equations depend not only on the rate of discharge and charge, but also on the depth of discharge when the charging process starts and on the degree of recharge finally reached, because of the decreasing charge acceptance of the battery with increasing state of charge. As a result, a high efficiency (a low charging factor) can be reached when, after a fairly deep discharge, the battery is reached only partially, since nearly all the current actually is reached. The charging efficiency is necessarily lower when the current is reached completely, since at the end the charging process, most of the current is used for water decomposition or the internal oxygen cycle.

Internal Resistance

The internal resistance of a battery is often quoted as a characteristic parameter.

A battery that is suitable for high-rate discharges must have a low internal resistance, otherwise the voltage drop caused by the current would limit the discharge too early.

Another field of application that makes use of the internal resistance is conductance measurements that during recent years attracted great attention as a tool to determine the state of valve-regulated lead-acid batteries in stationary applications.

The meaning of the terms ‘**internal resistance**’ has to be considered with some caution, because it is not a simple ohmic resistance.

Internal Resistance

- The charge-transfer step or the transfer reaction are characterized by the current/voltage curves or current/potential curves, discussed which do not lead to a linear relation between voltage and current. Consequently, the internal resistance, determined for a battery, is not an ohmic resistance, but depends on the current.
- The current/voltage curves are not symmetrical for the forward and backward reaction. As a consequence, the internal resistance usually is different for the discharging and charging reactions. Values quoted for the internal resistance in general concern the discharge of the battery
- The internal resistance depends on the state of charge of the battery
- The internal resistance is increased at reduced temperature owing to reduced conductivity and retarded kinetic parameters.

For these reason, the values quoted for the internal resistance of a battery can only be approximations that depends on the measuring method.

The Direct-current Method

The direct-current method is often applied in battery practice. With this method, the internal resistance (the d.c. resistance) of the battery is determined by measuring the terminal voltage at various loads. The battery is loaded with the current i_1 for a few seconds and he voltage E_1 is measured. Then the current is increased to the value i_2 and the battery voltage is reduced to the value E_2.

The R_i can be calculated according to the formula:

$$R_i = \frac{E_1 - E_2}{i_2 - i_1} = \frac{\Delta E}{\Delta i}$$

represents the usual method to determine an ohmic resistance, but in batteries the result depends on the current i_1 and i_2 that were applied, as well as on the difference Δi between the them. To achieve values for R_i that are relevant to practical applications, the currents i_1 and i_2 usually are specified and adapted to different battery types.

Short-Circuit Current

Short-circuit current flows when the two terminals of a cell or battery are (inadvertently) connected to each other. The short-circuit current is determined by the internal resistance of the cell or battery.

The short-circuit current represents a dynamic parameter that decreases quickly with proceeding discharge. Published values are always referred to the charged battery. The short-circuit current is (approximately) determined according to **Eq.** by extrapolating the resulting line to the voltage zero.

The short-circuit current represents the maximum current that could be supplied by the battery and could flow through the consuming device for a short period of time. The value of the short-circuit current helps in estimating the size of fuses to operate with the battery.

Alternating-Current Method; Cell Impedance; Cell Conductance

When an alternating current of sine-wave shape and the frequency ω flows through the battery the resulting complex resistance is composed of three components:

Components of the alternating resistance. i denotes the imaginary unit, CDL is caused by charge shifting within the double layer at the phase boundary between the active mterial and the electrolyte

	Resistance	**Conductance**
Ohmic Resistance	R	1/R
Inductance	iωL	1/iωL
Capacitance	$1/i\omega C_{DL}$	$i\omega C_{DL}$

The resulting resistance Z can be written as:

$$Z = \sqrt{R^2 + \left(i\omega L + \frac{1}{i\omega C_{DL}}\right)^2}$$

This is a complex resistance that depends on frequency

Alternating-Current Method; Cell Impedance; Cell Conductance

The inductance of batteries is very small (in the order of mH or even nH) and can usually be neglected.

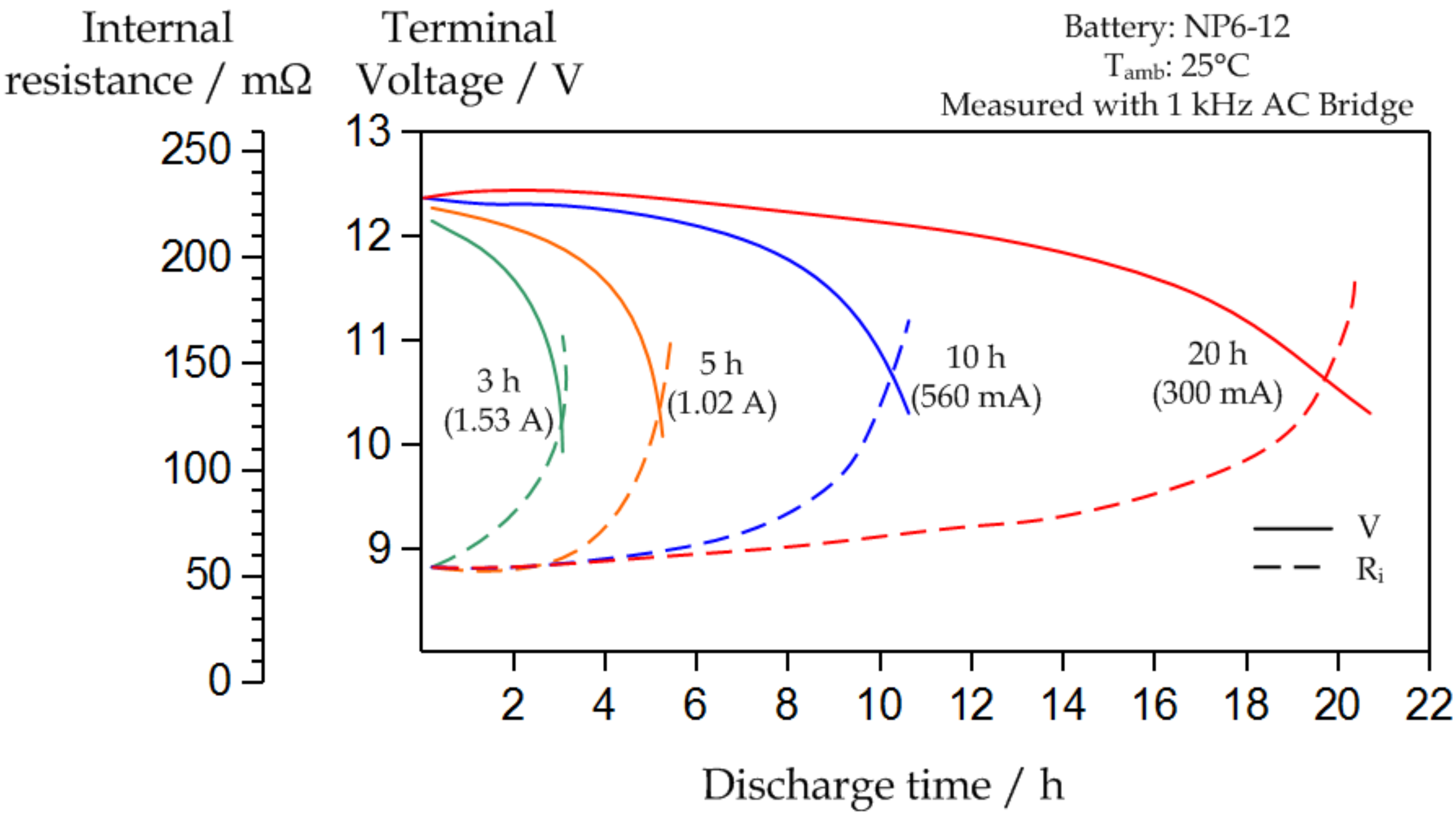
The double layer capacitance is quite high on account of the large surface area of the active material.

At a usual value of 10 μF·cm-2 of the true surface area, it amounts to the order of magnitude of Farads per Ah of battery capacity.

Often it cannot precisely be separated from the capacity caused by the electrochemical reactions

An advantage of a.c. method is that the battery is not discharged by the measurement!!

Discharge curves and internal resistance



Valve-regulated lead-acid battery. (YUASA NP Series)

Internal resistance of valve-regulated lead-acid batteries, all referred to 100 Ah of nominal capacity.

	Cylindrical	**Prismatic**		
	Pasted plates **Absorbent type** **2.5 – 5 Ah**	**Pasted plates** **Absorbent type** **10 – 100 Ah**	**Pasted plates** **Gel type** **50 – 100 Ah**	**Tubular plates** **Gel type** **100 – 3000 Ah**
mΩ/100 Ah	0.1 – 0.3	0.3 – 0.7	0.5 – 1.2	1 – 3

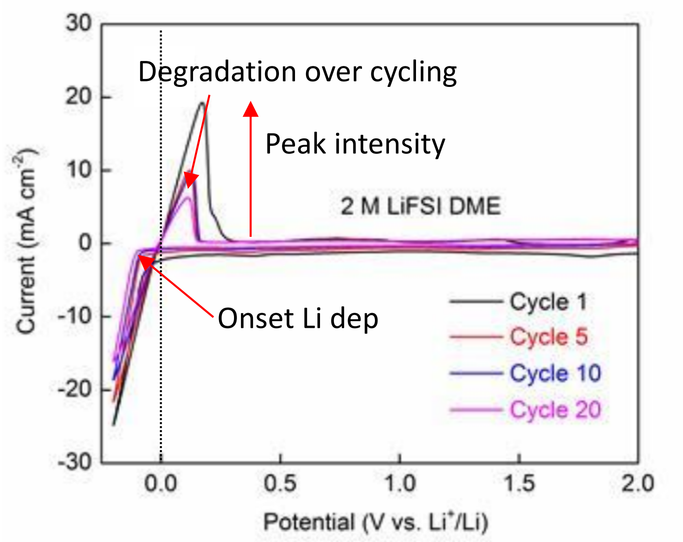
Internal resistance of sealed Ni/Cd batteries.

Cell condition: fully charged. (d.c.): values determined by Eq of R_i with $i_1=0.1C$ (A), $i_2 = 2.1C$(A) for button cells and $i_1=0.2C$ (A), $i_2=4.2C$(A) for cylindrical and prismatic cells. (a.c.): alternating-current method with 1000 Hz.

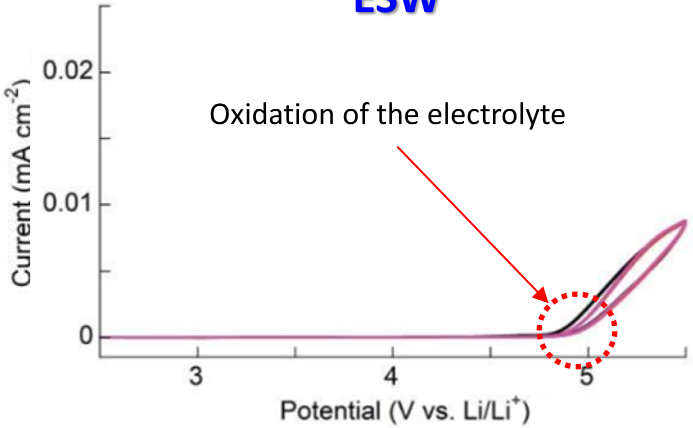
C / mΩ	**Button**			**Cylindrical**					**Prismatic**
	30 mAh	250 mAh	1000 mAh	250 mAh	1.2 Ah	1.2 Ah high rate	4 Ah	4 Ah high rate	15 Ah
d.c.	2200	300	50	58	19	12	7	4.5	2.5
a.c.	740	150	14	24	10	10	3.75	3.75	3.5

Focus on Electrochemistry

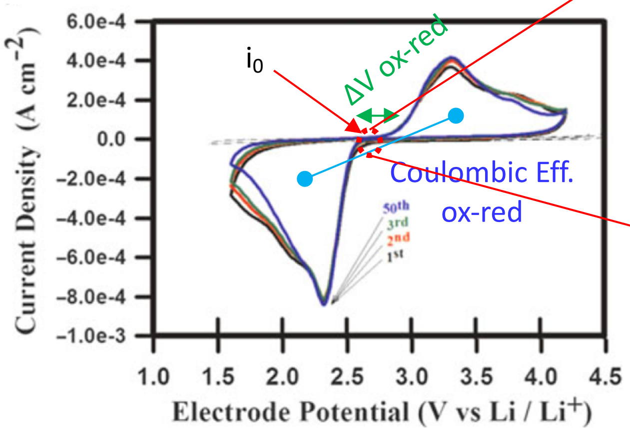
Li deposition and stripping

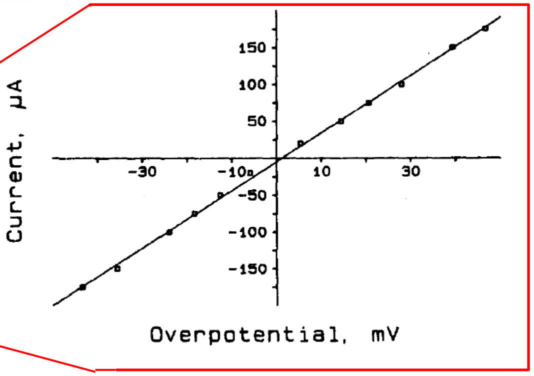


ESW



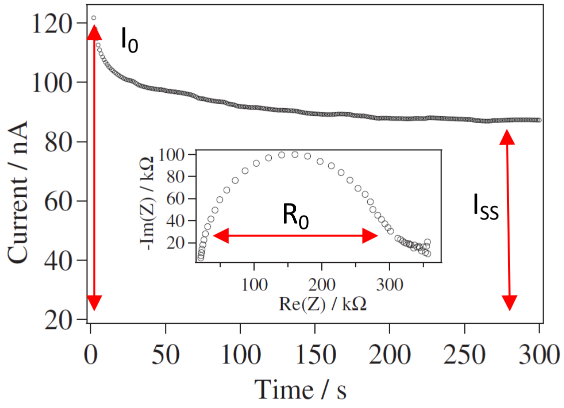
Li_2O_2 reversible formation





Li^+ transference number and conductivity

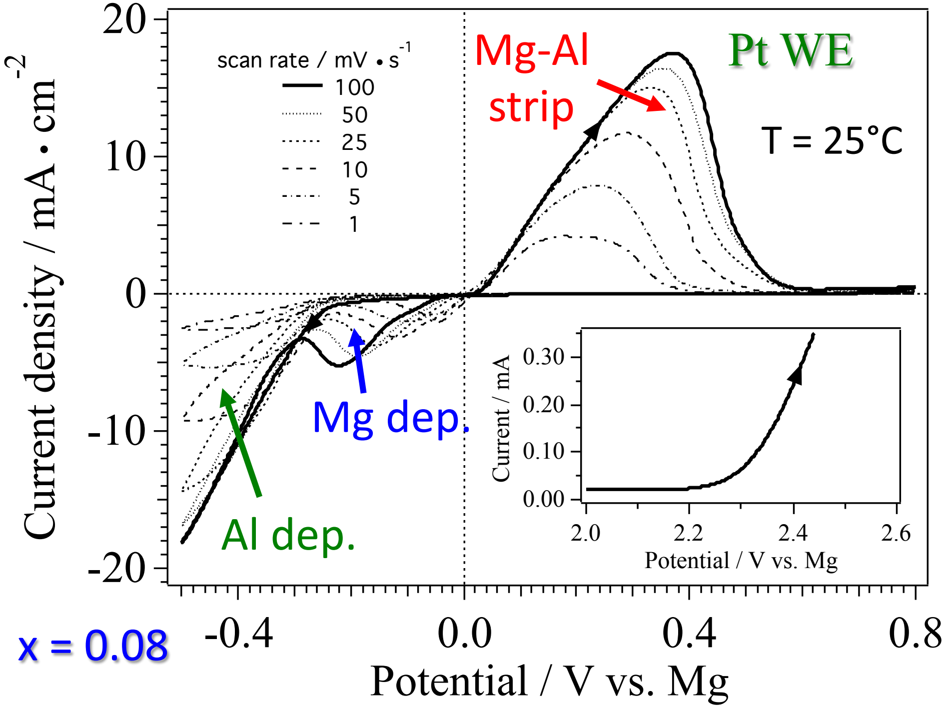
$$t_{Li^+} = \frac{I_{ss}(V - I_0 R_0)}{I_0(V - I_{ss} R_{ss})}$$

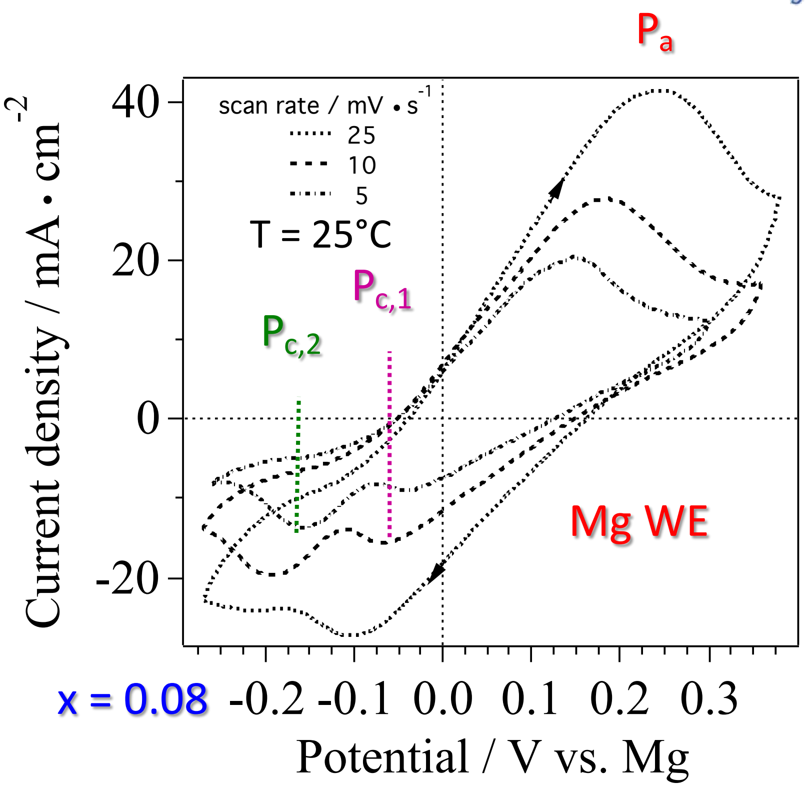


Polymer Electrolyte Reviews, MacCallum, J.R., Vincent, C.A. (Eds.), Springer Netherlands, 1989

J. Evans, C. A. Vincent, P. G. Bruce, Polymer 28 (1987) 2324.

Deposition and stripping of Mg/Al on Pt and Mg



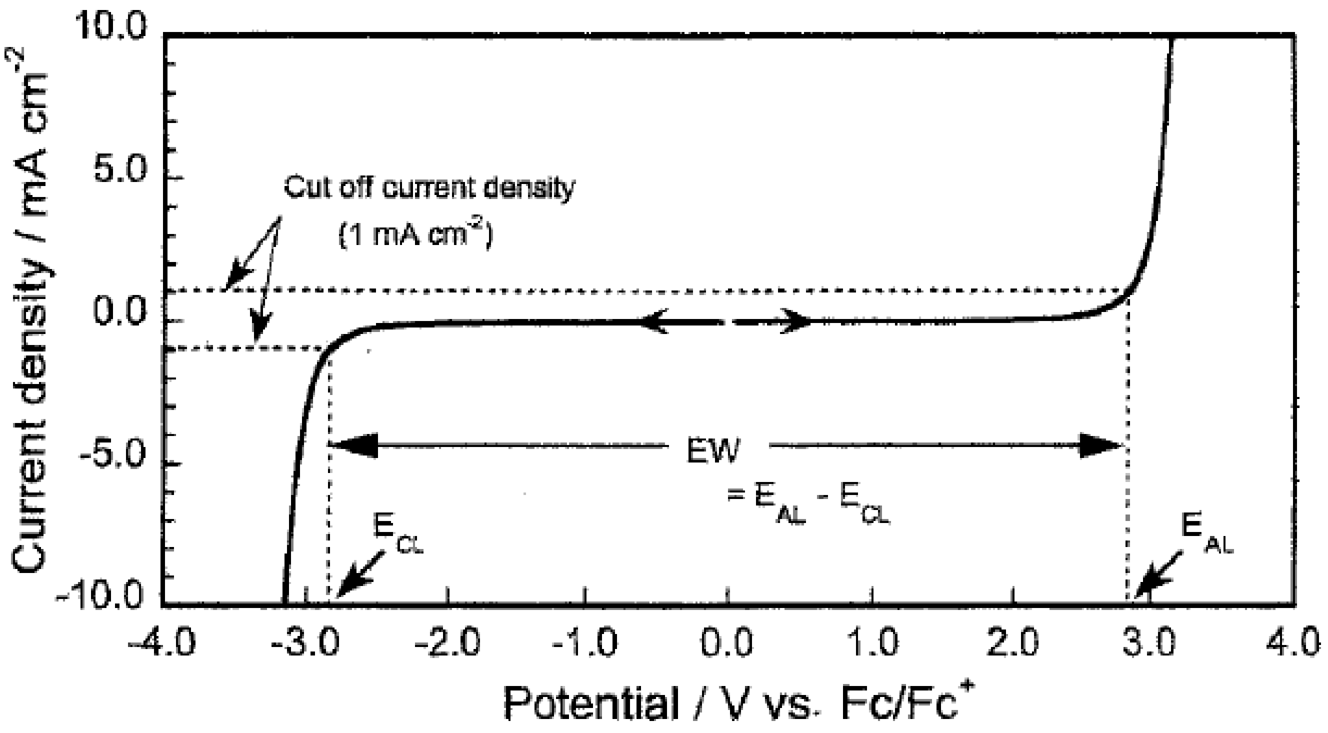


- The potential window of $[EMImCl/(AlCl_3)_{1.5}]/(\delta\text{-}MgCl_2)_x$ is ca. 2.3 V wide
- The anodic limit is the oxidation of $AlCl_4^-$, yielding Cl_2; the cathodic limit is set by electrolyte degradation[1].

- Mg deposition on a Mg WE occurs at two clearly distinct potential values, $P_{c,1}$ (-100 mV) and $P_{c,2}$ (-200 mV) , probably associated to I and II Mg oxidation states. The detailed assignment is still under investigation.

[1] P. Koronaios, R.A. Osteryoung, J. Electrochem. Soc. 146 (1999) 2995.

Electrochemical potential window



Typical linear-sweep voltammogramm of a room-temperature ionic liquid (RTIL).

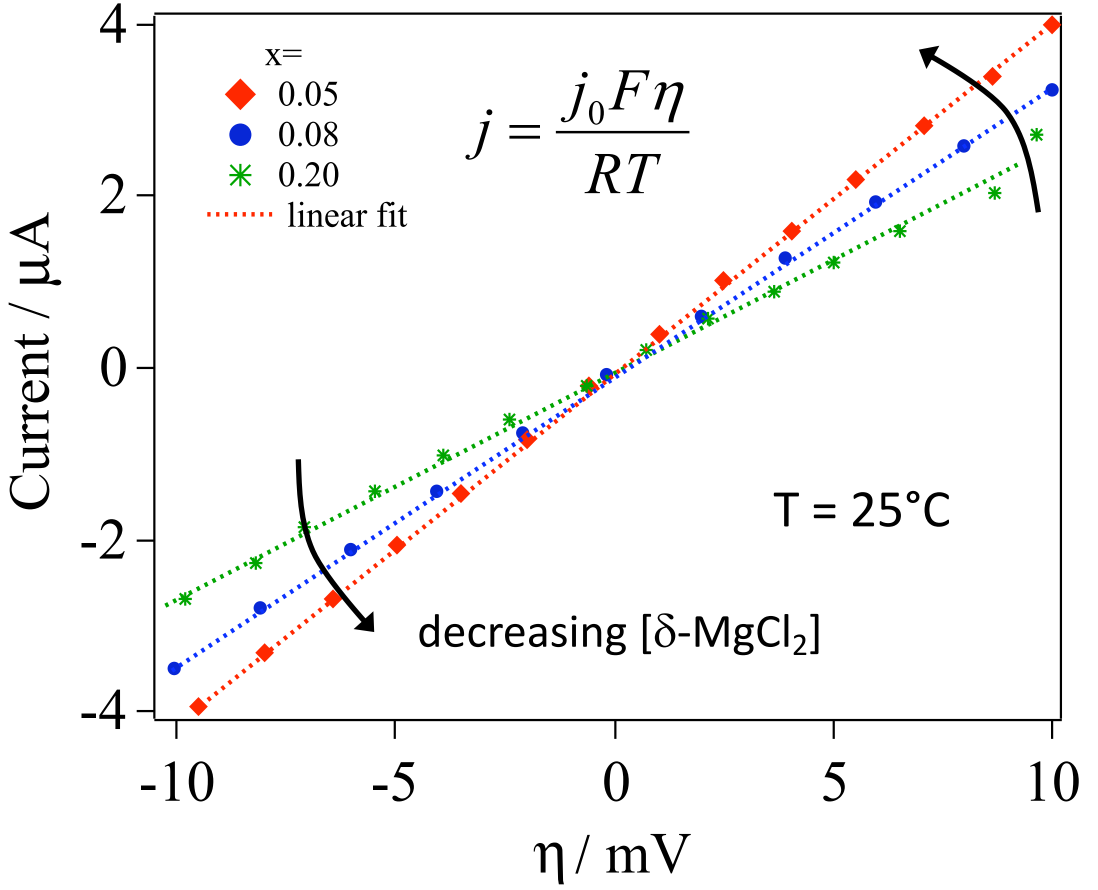
Electrochemical Aspects of Ionic Liquids, Hiroyuki Ohno Eds, A John Wiley & Sons, Inc., Hoboken, New Jersey (2005)

Exchange current density j_0

[EMImCl/$(AlCl_3)_{1.5}$]/$(\delta\text{-}MgCl_2)_x$

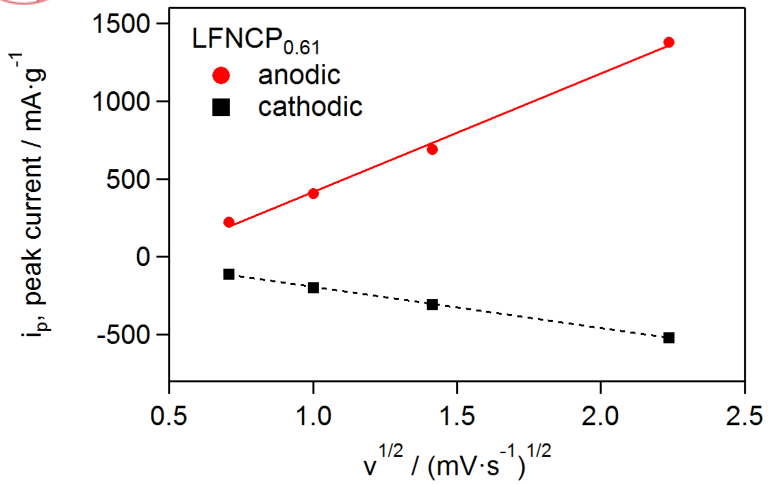
$x = n_{\delta\text{-}MgCl_2} / n_{IL}$	j_0 / mA·cm^{-2}
0	-
0.05	**1.68**
0.08	**0.79**
0.20	**0.54**

PEO($LiCF_3SO_3$) with EO/$LiCF_3SO_3$= 4
j_0 = 4.52 mA/cm² @ 140°C



$$j = \frac{j_0 F \eta}{RT}$$

Ex-situ electrochemistry: CV @RT



Randles-Sevcik equation[1-4]:

$$i_p = 0.4463\left(\frac{F^3}{RT}\right)^{1/2}\cdot n^{3/2}\cdot A\cdot \boxed{D_0^{1/2}}\cdot C_0^{*}\cdot v^{1/2}$$

$LFNCP_{0.61}$	D_{Li^+} anodic / $cm^2\cdot s^{-1}$	D_{Li^+} cathodic / $cm^2\cdot s^{-1}$
5.0 $mV\cdot s^{-1}$	5.14E-10	7.31E-11
2.0 $mV\cdot s^{-1}$	3.24E-10	6.44E-11
1.0 $mV\cdot s^{-1}$	2.22E-10	5.29E-11
0.5 $mV\cdot s^{-1}$	1.34E-10	3.40E-11
average	2.98E-10	5.61E-11

cathodic	$LFNCP_{0.00}$	$LFNCP_{0.12}$	$LFNCP_{0.32}$	$LFNCP_{0.50}$	$LFNCP_{0.61}$
$D_{Li,average}$ / $cm^2\cdot s^{-1}$	1.65E-11	1.43E-11	2.70E-11	1.84E-11	5.61E-11

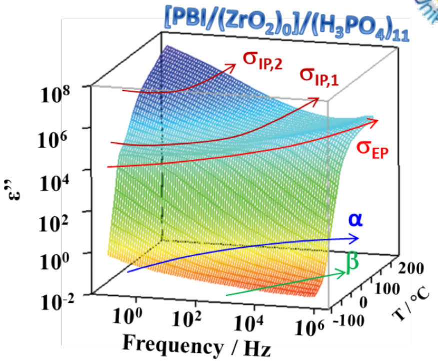
increasing [Co] →

- In accordance with a diffusion-controlled process, the **intensity of CV peaks (i_p) are linearly dependent on the square root of the scan rates**;
- Fitting i_p *vs.* $v^{1/2}$ using the Randles-Sevcik equation allows to calculate the lithium ion diffusion coefficients;
- D_{Li^+} are coherent with values reported in the literature[5];
- With respect to the extraction event, the **Li^+ insertion process in $LFNCP_x$ is kinetically inhibited**; the D_{Li^+} values in cathodic reactions are lower than that of anodic processes;

[1] X.H. Rui et al., *Electrochim. Acta* **2010**, *55*, 2384
[2] S.B. Tang et al., *Mater. Chem. And Phys.* **2008**, *11*, 149
[3] N. Ding et al., *Solid State Ionics* **2009**, *180*, 222
[4] J. Xie et al., *Solid State Ionics* **2008**, *179*, 362
[5] J. Xie et al., *J. Power Sources* **2009**, 192, 689

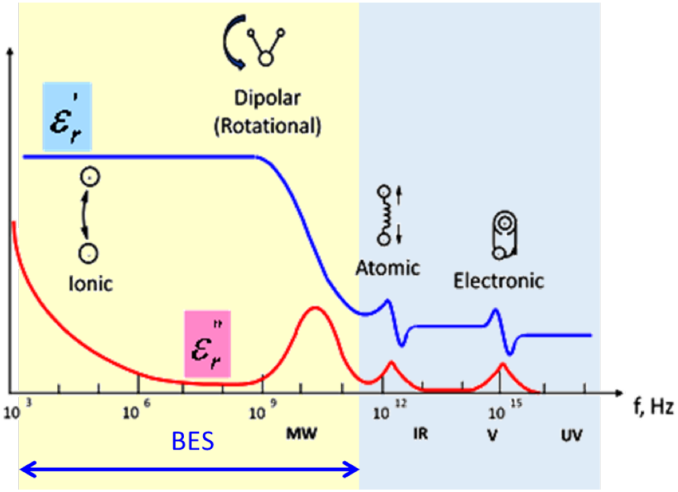
Electric Response: BES

- **Why?**
  - ❖ *A variety of physical phenomena can be studied including interphase boundaries, phase transitions, and electrical relaxations*.



- **Where?**
  - ❖ **Electrolyte** → the **conductivity and charge conduction mechanism** can be studied at a high level of detail, also as a function of the temperature (123 ÷ 523 K).

- **How?**
  - ❖ An oscillating electric field is applied between two electrodes with a modulated frequency;
  - ❖ The output current I(t) is out of phase with respect to the applied voltage U(t) by an angle ϕ (*$I(t)=I_0\cos(\omega t+\varphi)$*);
  - ❖ ω is varied and the instrumentation detects the current I(t) value at each frequency;



- ❖ The electric response under different representations (ε*, σ*, and tanδ) are fitted using a suitable equation;
- ❖ Information about polarizations and relaxations elucidates the conductivity mechanism of the material.

BES Studies

An extensive study of the electrical response and conductivity mechanism of IL is performed by analyzing the real and imaginary components of complex conductivity and permittivity spectra in terms of:

- **Dielectric relaxation events;**
- **Polarization phenomena.**

The **conductivity and the electric response** are investigated by **BES**:

- in the *f* and T range of 0.01 Hz ÷ 20 GHz and -150 ÷ 400°C, respectively.
- at 80°C in the *f* and P_{CO_2} range of 20 ÷ 10^6 Hz and 1 ÷ 130 bar, respectively.

Complex conductivity
σ(ω)*

$$\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega)$$

Complex permittivity
ε(ω)*

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

with

$$\sigma^*(\omega) = i\omega\varepsilon_0\varepsilon^*(\omega) = \frac{1}{\rho^*(\omega)} = \frac{1}{kZ^*(\omega)}$$

ρ(ω) is the complex resistivity and k = A/d is the geometric cell constant. A is the area of the electrode and d is the sample thickness.

Fundamentals: Electrical Response

It is obtained: $\vec{J}(\omega)=i\omega\varepsilon_m^*(\omega)\varepsilon_0\vec{E}(\omega)$

Which corresponds to Ohm's Law: $\vec{J}(\omega)=\sigma_m(\omega)\vec{E}(\omega)$

$$\Longrightarrow \quad \vec{J}(\omega)=i\omega\varepsilon_0\varepsilon_m^*(\omega)\vec{E}(\omega)=\sigma_m^*(\omega)\vec{E}(\omega)$$

Therefore

$$\boxed{\sigma_m^*(\omega)=i\omega\varepsilon_0\varepsilon_m^*(\omega)} \Longrightarrow \boxed{\begin{aligned}\sigma'_m(\omega)&=\omega\varepsilon_0\varepsilon''_m(\omega)\\ \sigma''_m(\omega)&=\omega\varepsilon_0\varepsilon'_m(\omega)\end{aligned}}$$

Considering:

$$\sigma_m^*(\omega)=\frac{1}{\rho^*(\omega)}=\frac{1}{KZ^*(\omega)}$$

where $\rho^*(\omega)$ and $Z^*(\omega)$ are the complex resistivity and impedance spectra, respectively

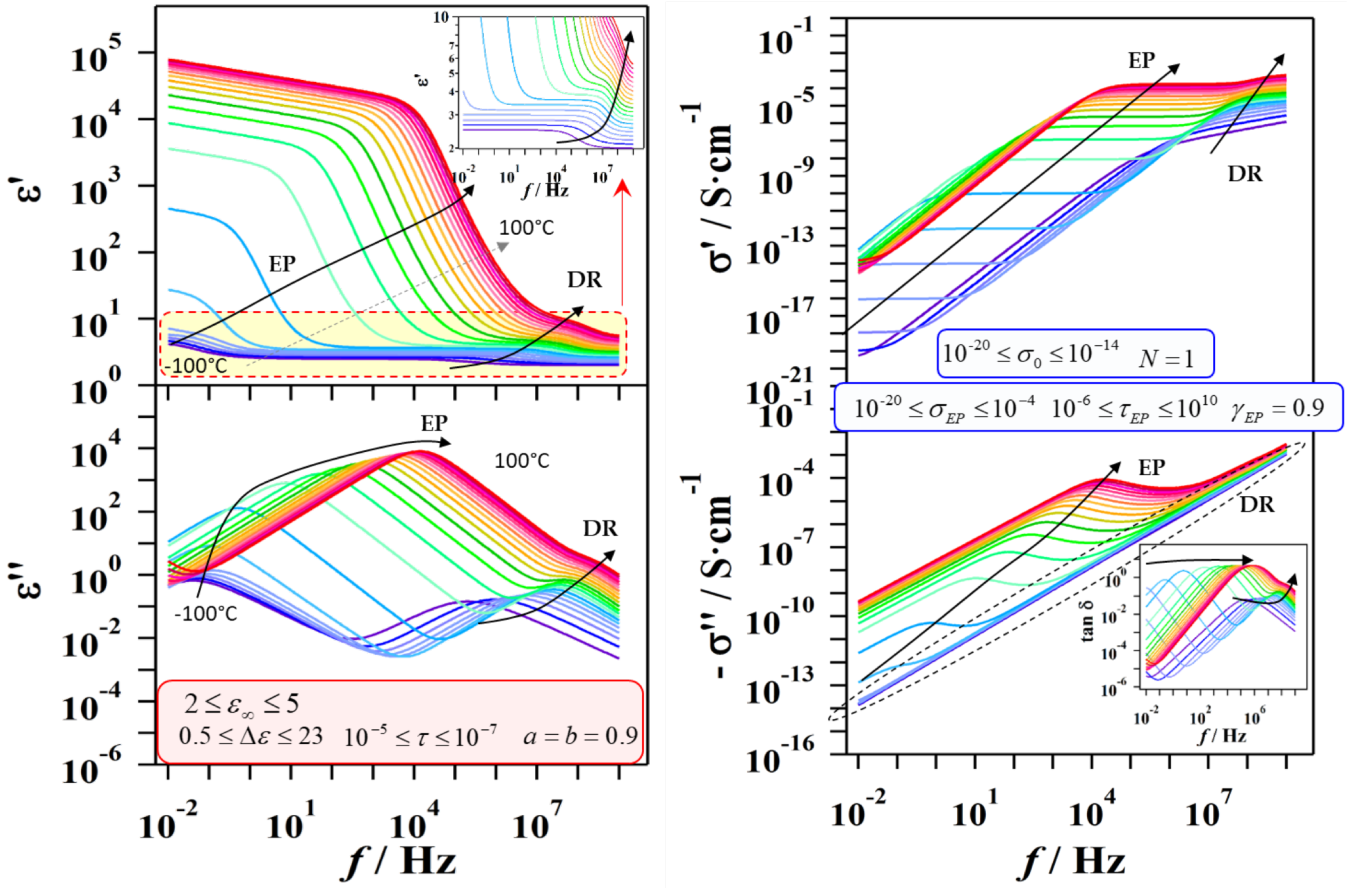
$$\sigma'_m(\omega)=\frac{Z'(\omega)}{K\left[\left(Z'(\omega)\right)^2+\left(Z''(\omega)\right)^2\right]^{1/2}}$$

$$\sigma''_m(\omega)=\frac{Z''(\omega)}{K\left[\left(Z'(\omega)\right)^2+\left(Z''(\omega)\right)^2\right]^{1/2}}$$

σ_m / S·cm^{-1}	**Type of material**	**Preferred representation**
$10^1 - 10^{-2}$	Conductor	$\sigma^*(\omega) > Z^*(\omega)$
$10^{-2} - 10^{-6}$	Semiconductor	$Z^*(\omega) > \sigma^*(\omega) > \varepsilon^*(\omega)$
$10^{-5} - 10^{-14}$	Dielectrics	$\varepsilon^*(\omega) > \sigma^*(\omega)$

Di Noto, V. J. Phys. Chem. B 2000, 104, 10116.
Di Noto, V.;et al. J. Phys. Chem. B 2004, 108, 18832.

Focus on BES 1



$10^{-20} \le \sigma_0 \le 10^{-14} \quad N = 1$

$10^{-20} \le \sigma_{EP} \le 10^{-4} \quad 10^{-6} \le \tau_{EP} \le 10^{10} \quad \gamma_{EP} = 0.9$

$2 \le \varepsilon_\infty \le 5$

$0.5 \le \Delta\varepsilon \le 23 \quad 10^{-5} \le \tau \le 10^{-7} \quad a = b = 0.9$

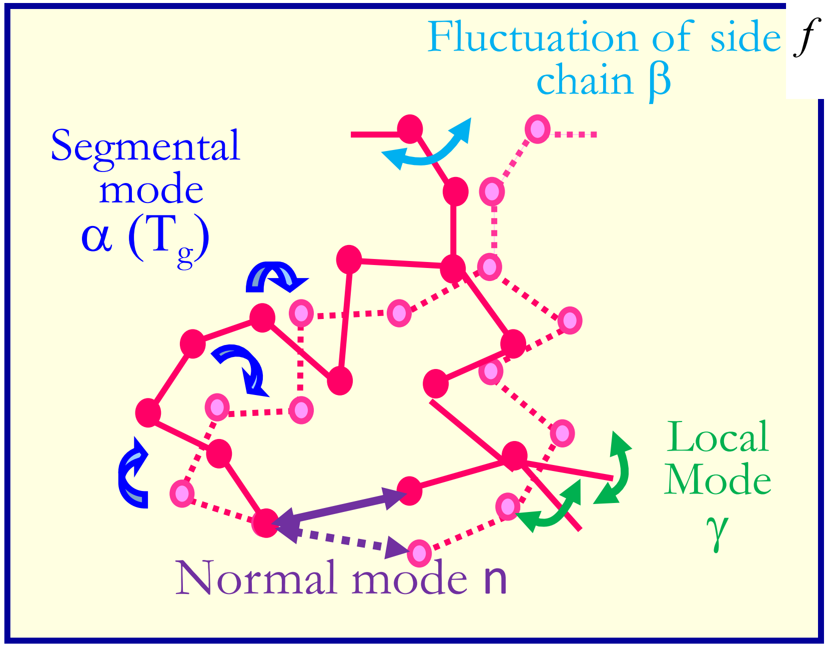
$$\varepsilon_m^*(\omega) = -i\left(\frac{\sigma_0}{\omega\varepsilon_0}\right)^N + \frac{\sigma_{EP}(i\omega\tau_{EP})^{\gamma_{EP}}}{i\omega\varepsilon_0\left[1+(i\omega\tau_{EP})^{\gamma_{EP}}\right]} + \sum_{j=1}^{n}\frac{\sigma_{IP,j}(i\omega\tau_{IP,j})^{\gamma_{IP,j}}}{i\omega\varepsilon_0\left[1+(i\omega\tau_{IP,j})^{\gamma_{IP,j}}\right]} + \sum_{k=1}^{m}\frac{\Delta\varepsilon_k}{\left[1+(i\omega\tau_k)^{a_k}\right]^{b_k}} + \varepsilon_\infty$$

Interdomain polarization (IP)

Electrode polarization (EP)

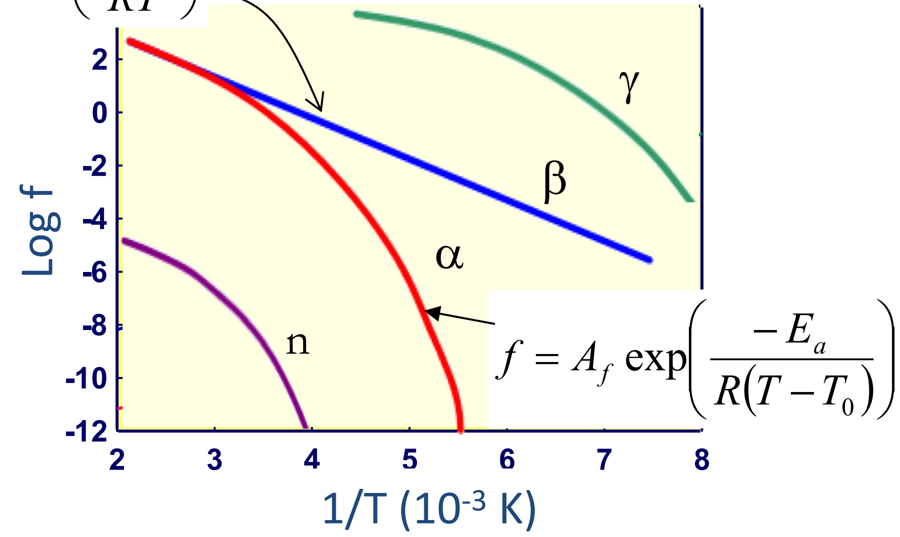
Dielectric relaxations (DR)

Dielectric Relaxations in Polymers



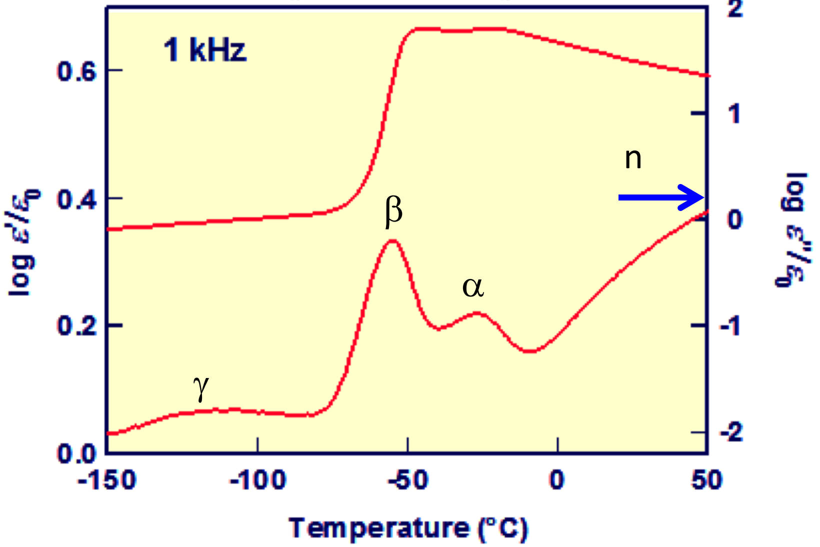
Transition Map

$$f = A_f \exp\left(\frac{-E_a}{RT}\right)$$

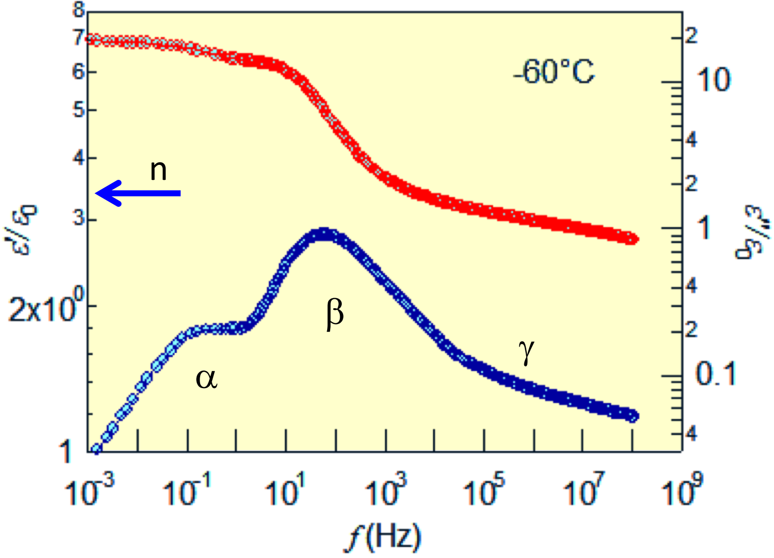


$$f = A_f \exp\left(\frac{-E_a}{R(T-T_0)}\right)$$

Temperature Spectra



Frequency Spectra

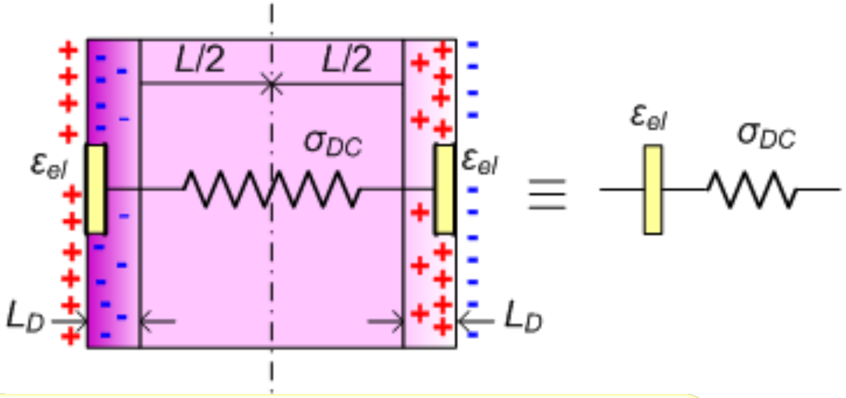


Fundamentals: Electrode Polarization[1-4]

For conducting materials, the electric response as a function of ω of the EP event:

$$\sigma^*_{EP}(\omega)=\frac{1}{1/\sigma_{\mathrm{EP}}+1/i\omega\varepsilon^*_{el}(\omega)}$$

$$\varepsilon^*_{el}=\varepsilon_{EP}(i\omega)^{\gamma-1}$$



$$\sigma^*_{EP}(\omega)=\frac{\sigma_{\mathrm{EP}}(i\omega\tau_{\mathrm{EP}})^{\gamma_{\mathrm{EP}}}}{1+(i\omega\tau_{\mathrm{EP}})^{\gamma_{\mathrm{EP}}}} \qquad \varepsilon^*_{EP}(\omega)=\frac{\sigma_{\mathrm{EP}}(i\omega\tau_{\mathrm{EP}})^{\gamma}}{i\omega\left(1+(i\omega\tau_{\mathrm{EP}})^{\gamma}\right)} \quad \text{with} \quad \tau_{EP}=(\varepsilon_{EP}/\sigma_{EP})^{1/\gamma_{EP}}$$

$\sigma^*_{\mathrm{EP}}(\omega)$ results in a Cole-Cole type conductive function with a relaxation time τ_{EP} and a parameter γ_{EP} corresponding to the distribution of relaxation times.

$$\tau_{EP}=M\tau=\frac{L}{2\mu}\left(\frac{\varepsilon_{\mathrm{r}}\varepsilon_0}{\rho_0 kT}\right)^{1/2} \qquad \text{where} \qquad M=\frac{(L/2)}{L_D}=q\frac{L}{2}\left(\frac{\rho_0}{\varepsilon_{\mathrm{r}}\varepsilon_0 kT}\right)^{1/2}$$

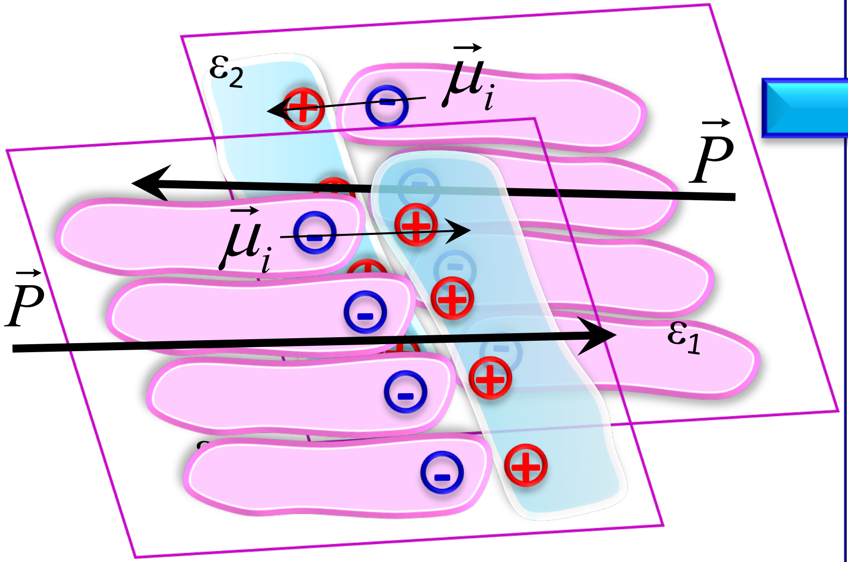
Charge mobility

Charge density

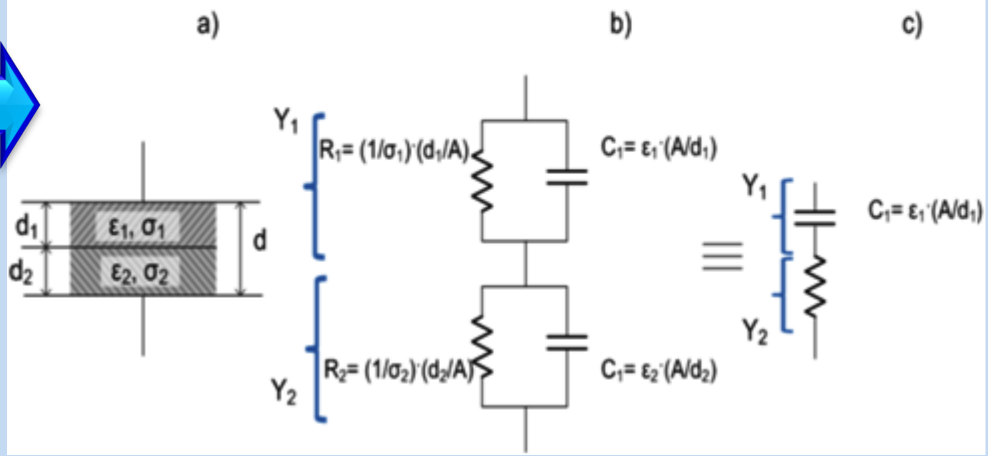
EP can be discriminated from the bulk relaxations of the sample by studying the effect of changing the electrode materials and the sample thickness on τ_{EP}.

[1] Furukawa, *et al.,*. *J. Appl. Phys., Part 1* **1997**, *36*, 1119.
[2] Kano, K.; *et al., J. Appl. Phys., Part 1* **2001**, *40*, 3246.
[3] Furukawa, T. *et al.,* Y. *IEEE T. Dielect. El. In.* **2004**, *11*, 65.
[4] Johnson, J. F.; Cole, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 4536.
[5] Klein, R. J.; et al., J. Chem. Phys. 2006, 124, 144903.
[6] V. Di Noto; et al. In "Solid State Proton Conductors: Properties and Applications in Fuel Cells", Eds P. Knauth and M.L. Di Vona, Chap. 5, J. Wiley and Sons, Ltd, 2012.

Fundamentals: Interdomain Polarization



$$\vec{P} = \sum_i \vec{\mu}_i$$



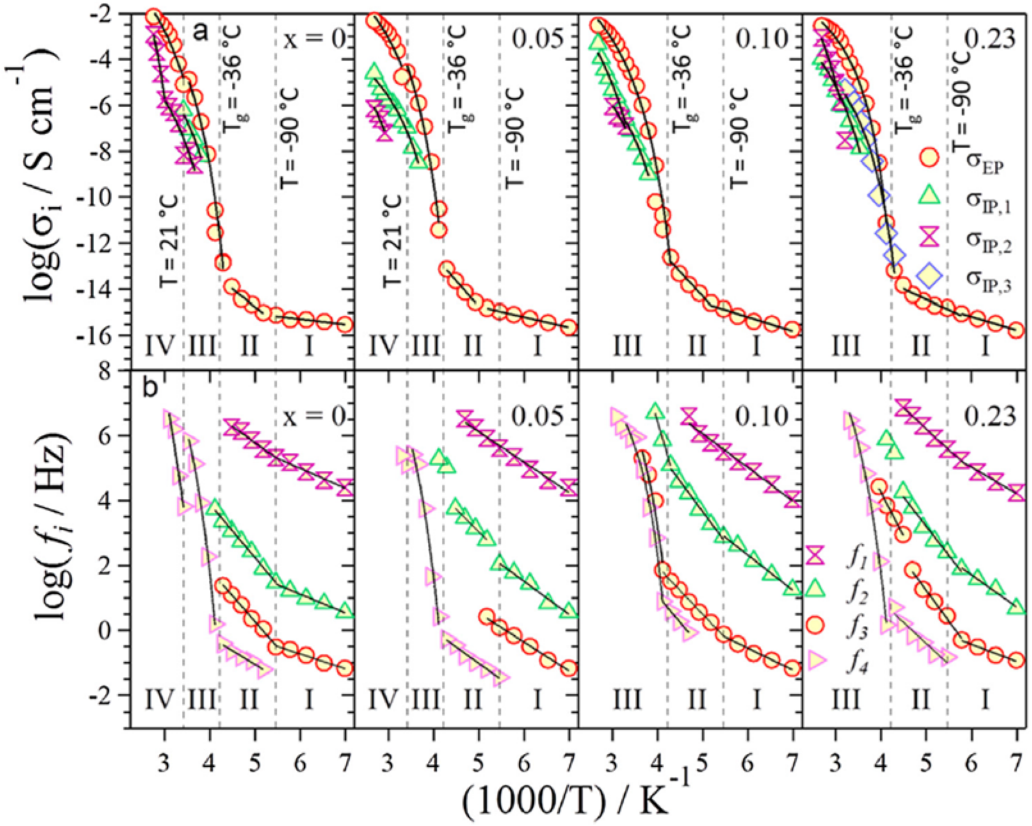
a) Two layer model of interdomain polarization
b) Complete equivalent circuit of the system a)
c) equivalent circuit when $\varepsilon_1/d_1 >> \varepsilon_2/d_2$, $\varepsilon_o\varepsilon_1 >> \sigma_2$, $\sigma_2 >> \varepsilon_2\varepsilon_o$, and $\sigma_2 >> \sigma_2$. Y_1 and Y_2 are the admittances of 1 and 2 parallel equivalent circuits.

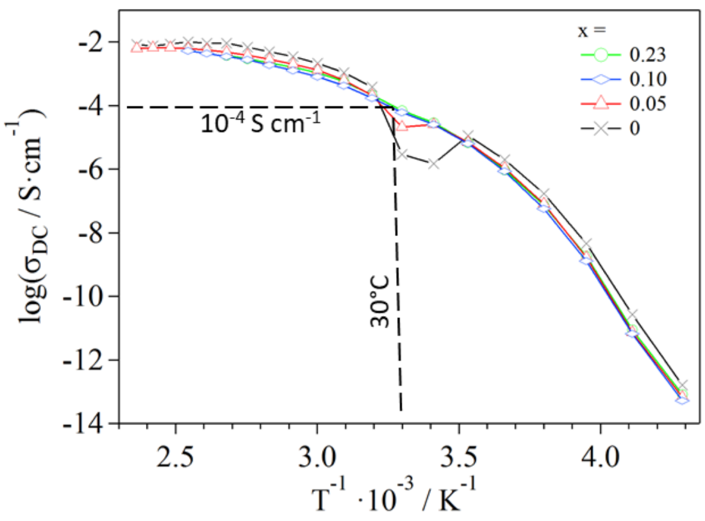
$$\varepsilon^*_{IP} = \frac{\sigma_{IP}}{i\omega\varepsilon_0} \frac{(i\omega\tau_{IP})^{\gamma_{IP}}}{\left[1+(i\omega\tau_{IP})^{\gamma_{IP}}\right]} \qquad \tau_{IP} = \left(\frac{\varepsilon_{IP}}{\sigma_{IP}}\right)^{\frac{1}{\gamma_{IP}}}$$

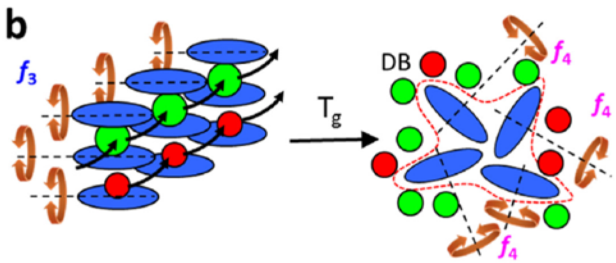
The relaxation time decreases as the conductivity of the highest conducting nanodomains increases.

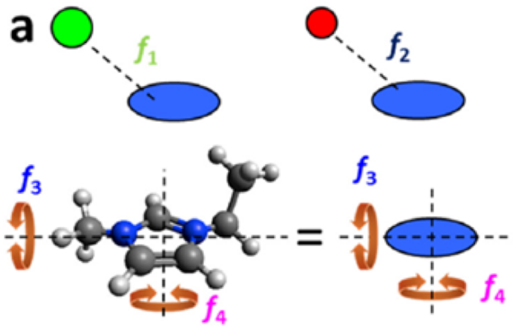
V. Di Noto, G.A. Giffin, K. Vezzù, M. Piga, S. Lavina, In "Solid State Proton Conductors: Properties and Applications in Fuel Cells", Eds P. Knauth and M.L. Di Vona, Chap. 5, J. Wiley and Sons, Ltd, 2012.

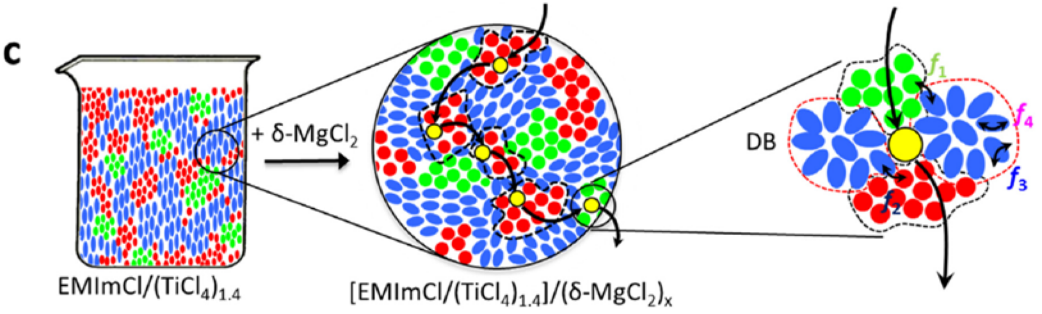
Focus on BES 2











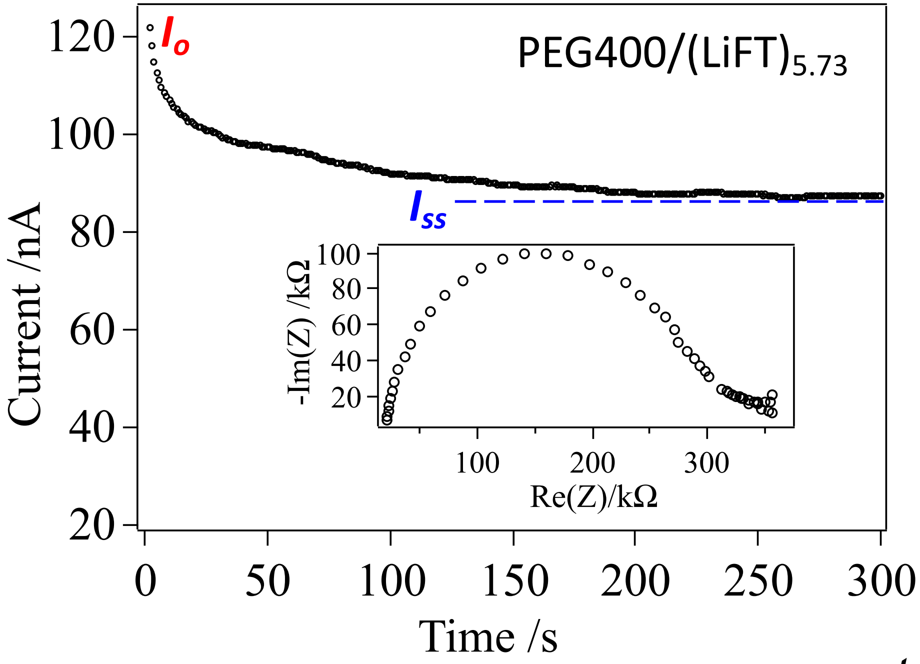
$EMImCl/(TiCl_4)_{1.4}$

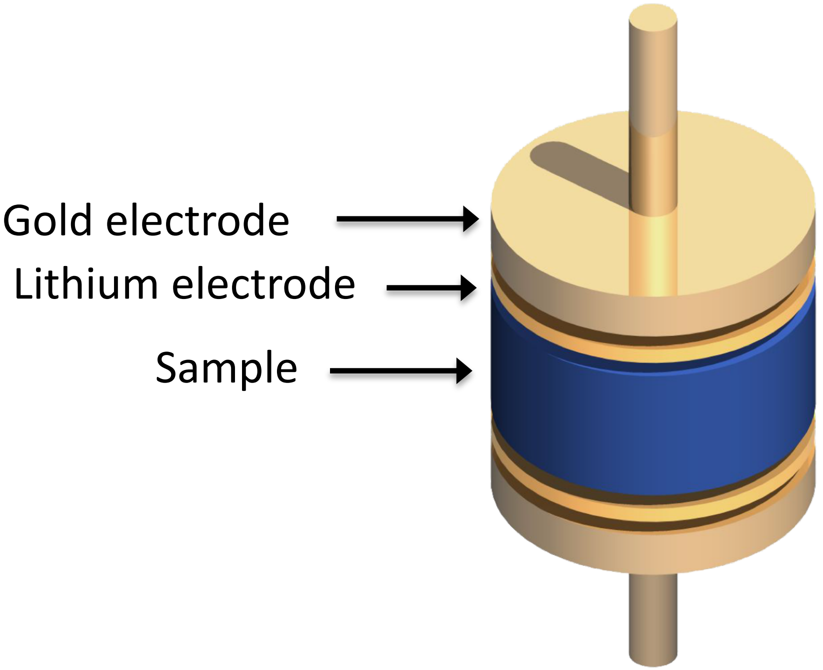
$[EMImCl/(TiCl_4)_{1.4}]/(\delta\text{-}MgCl_2)_x$

🔴 = $TiCl_6^{2-}$
🟢 = $Ti_2Cl_9^-$
🔵 = $EMIm^+$
🟡 = Mg-based species

[1] V. Di Noto *et al*. Electrochim. Acta 246 (2017) 914-923.

Transference number measurement[1]





Gold electrode

Lithium electrode

Sample

	t_{Li}
PEG400/(LiFT)$_{2.80}$ (after 6h stabilization @ 60°C)	1.00
PEG400/(LiFT)$_{5.73}$ (after 6h stabilization @ 60°C)	0.99

$$t_{Li^+} = \frac{I_{ss}(V - I_0 R_0)}{I_0(V - I_{ss} R_{ss})}$$

I_{ss}=steady state current
I_0=initial current
R_0=resistance of the passivation layer
R_{ss}=resistance of the passivation layer (s.s.)

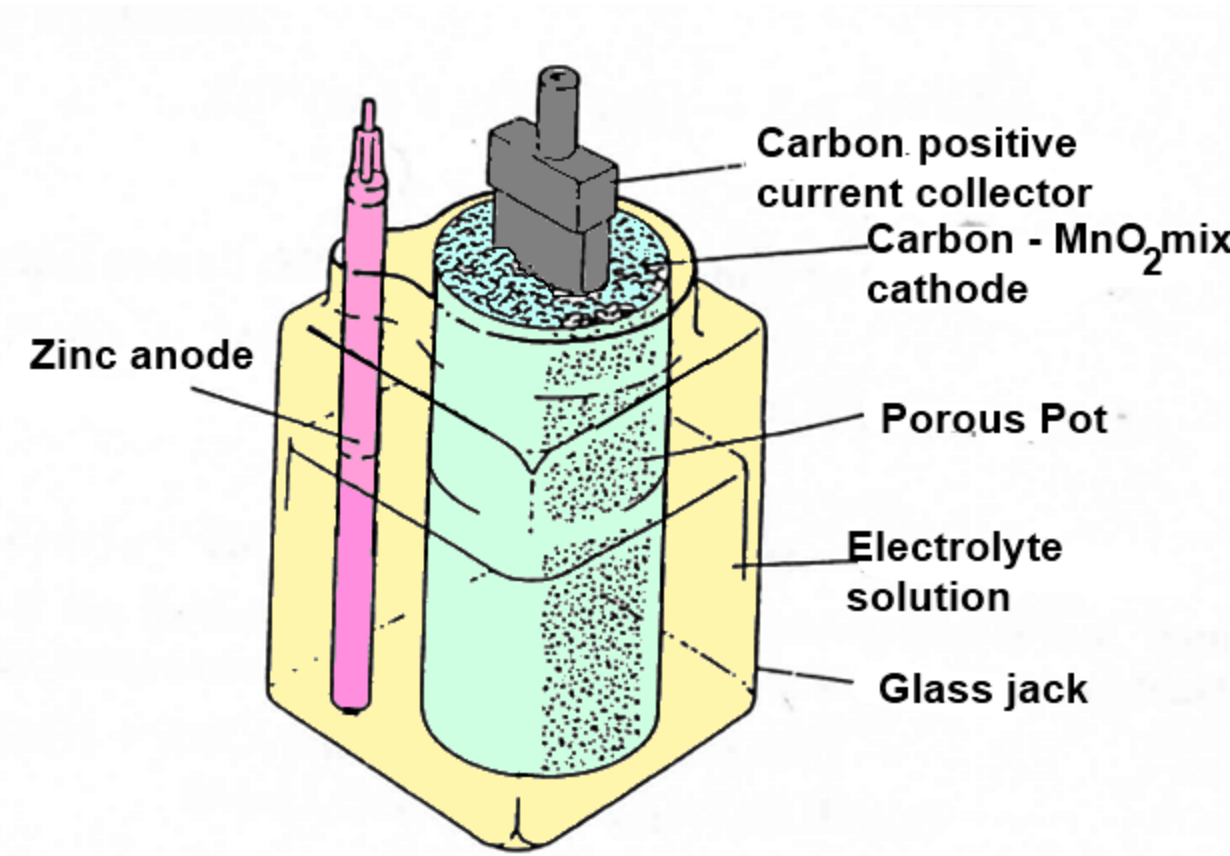
[1] J. Evans, C. A. Vincent and P. G. Bruce Polymer 28 (1987) 2324

Primary aqueous electrolyte cells

The Leclanché cell may be written as

$$Zn_{(s)}\left|ZnCl_{2,(aq)}, NH_4Cl_{(aq)}\right|MnO_{2,(s)}, C_{(s)}$$

and the OCV* is in the range 1.55-1.74 V. Despite the many advantages which have brought this cell to a high degree of reliability and greatly improved performance, the electrochemical system of the modern cell is basically the same as that proposed by George Leclanché in 1866.



Schematic view of the original Leclanché wet cell

Discharge Mechanisms

The discharge mechanism of the Leclanché cell is complex and not all the details are yet fully understood. The basic process consists of oxidation of Zinc at the anode to form zinc ions in solution:

$$\mathrm{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}$$

Together with a reduction of Mn(IV) to a trivalent state as $MnO \cdot OH(s)$ or $Mn_2O_3 \cdot H_2O(s)$, at the cathode, e.g.

$$2MnO_{2,(s)} + 2H_2O + 2e^- \rightarrow 2MnO \cdot OH_{(s)} + 2OH^-_{(aq)}$$

The initial products of the electrode reactions may then undergo further reactions in solution. The prevailing process is:

$$Zn^{2+}_{(aq)} + 2OH^-_{(aq)} + 2NH^+_{4,(aq)} \rightarrow Zn(NH_3)^{2+}_{2,(aq)} + 2H_2O$$

Followed by the formation of the slightly soluble $Zn(NH_3)_2Cl_2$:

$$Zn(NH_3)^{2+}_{2,(aq)} + 2Cl^-_{(aq)} \rightarrow Zn(NH_3)_2Cl_{2,(s)}$$

Discharge Mechanisms

For light discharges and with certain oxides an alternative reaction is:

$$Zn^{2+}_{(aq)} + 2MnO \cdot OH_{(s)} \rightarrow ZnO \cdot Mn_2O_{3,(s)} + 2H_2O$$

At lower NH_4^+ concentrations, the zinc ions precipitate out as one or more oxychloride species: e.g.

$$5Zn^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + 8OH^{-}_{(aq)} \rightarrow ZnCl_2 \cdot 4Zn(OH)_{2,(s)}$$

or as the hydroxide:

$$Zn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Zn(OH)_{2,(s)}$$

The principal overall cell reactions can therefore be summarized as:

$$Zn_{(s)} + 2MnO_{2,(s)} + 2NH_4Cl_{(aq)} \rightarrow 2MnO \cdot OH_{(s)} + Zn(NH_3)_2Cl_{2,(s)}$$

$$Zn_{(s)} + 2MnO_{2,(s)} \rightarrow ZnO \cdot Mn_2O_{3,(s)}$$

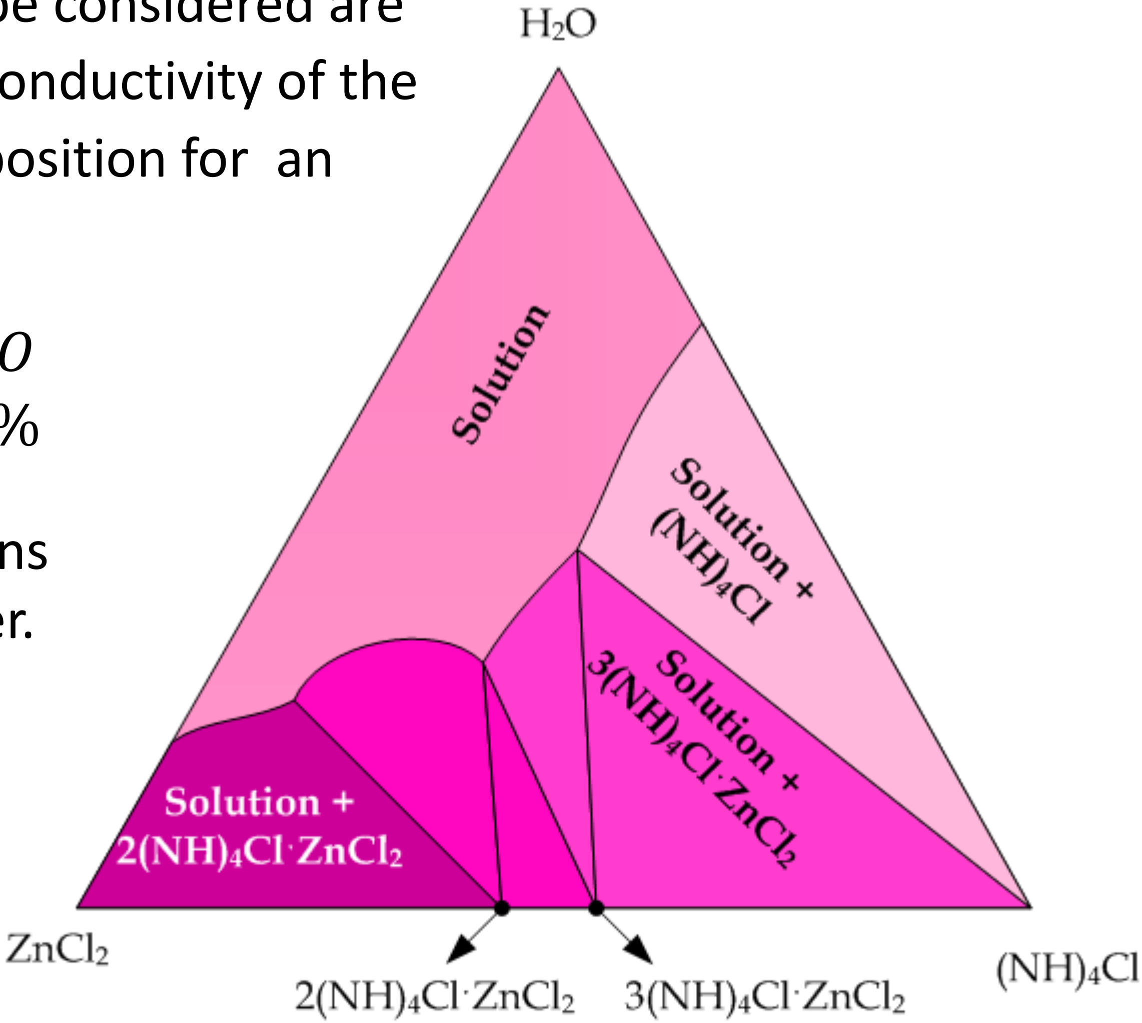
Electrolyte

The electrolyte in the original Leclanché cell was a saturated solution of ammonium chloride.

The important variable to be considered are the composition, pH and conductivity of the electrolyte. A typical composition for an undischarged cell is:

NH_4Cl	$ZnCl_2$	H_2O
28%	16%	56%

although there are variations depending on manufacturer.



Schematic ternary phase diagram for the system $ZnCl_2$–NH_4Cl–H_2O at T_{amb}.

Electrolyte

Since the basic cathode reaction involves the production of OH^- ions, the resulting increase in pH causes the formation of ammonia, which in turn complexes with zinc ions.

$$Zn^{2+}_{(aq)} + 2Cl^-_{(aq)} \xrightarrow{2NH_3} \underset{\textbf{Slightly soluble}}{Zn(NH_3)_2Cl_2} \xrightarrow{2NH_3} Zn(NH_3)^{2+}_{4,(aq)} + 2Cl^-_{(aq)}$$

The formation of these complexes serves to buffer the rise pH due to the cathodic discharge process. Precipitation of $Zn(NH_3)Cl_2$ has the effect of increasing cell resistance.

In the anodic region, the concentration of Zn^{2+} ions increases as discharge proceeds, leading to a decrease in pH due to hydrolytic reactions of the type:

$$Zn^{2+}_{(aq)} + H_2O \rightarrow Zn(OH)^+_{(aq)} + H^+_{(aq)}$$

A pH gradient is thus established during cell discharge.

Cathode

The cathode ‘mix’ consists basically of **manganese dioxide to which carbon, in finely divided form** (e.g. as acetylene black), has been added in order to provide an adequate electronic conductivity.

The current collector is generally also made of **carbon**, in the form of either **a rod or a thin sheet**.

The active material is the **MnO_2** and it was realized from early in the development of the Leclanché cell that use of naturally occurring MnO_2 from ***different sources produced striking variations in cell performance***. Even now, when synthetic MnO_2 is used in almost all high performance batteries, slight changes in the method of preparation can have significant effects.

MnO_2 has **numerous allotropic forms**, with subtle crystal structure modifications and a wide variety of surface types. ***So far it has not proved possible to relate in any exact way the crystal structure, surface properties, etc. of a particular sample of MnO_2.***

Cathode

The overall cathodic reaction in which $MnO_{2,(s)}$ is reduced to $MnO·OH_{(s)}$ is now known to involve a solid state diffusion process in which protons are transported from the surface to the interior of the MnO_2 grains:

$$H_2O \rightleftharpoons H^+_{(surface\ )} + OH^-_{(aq}$$

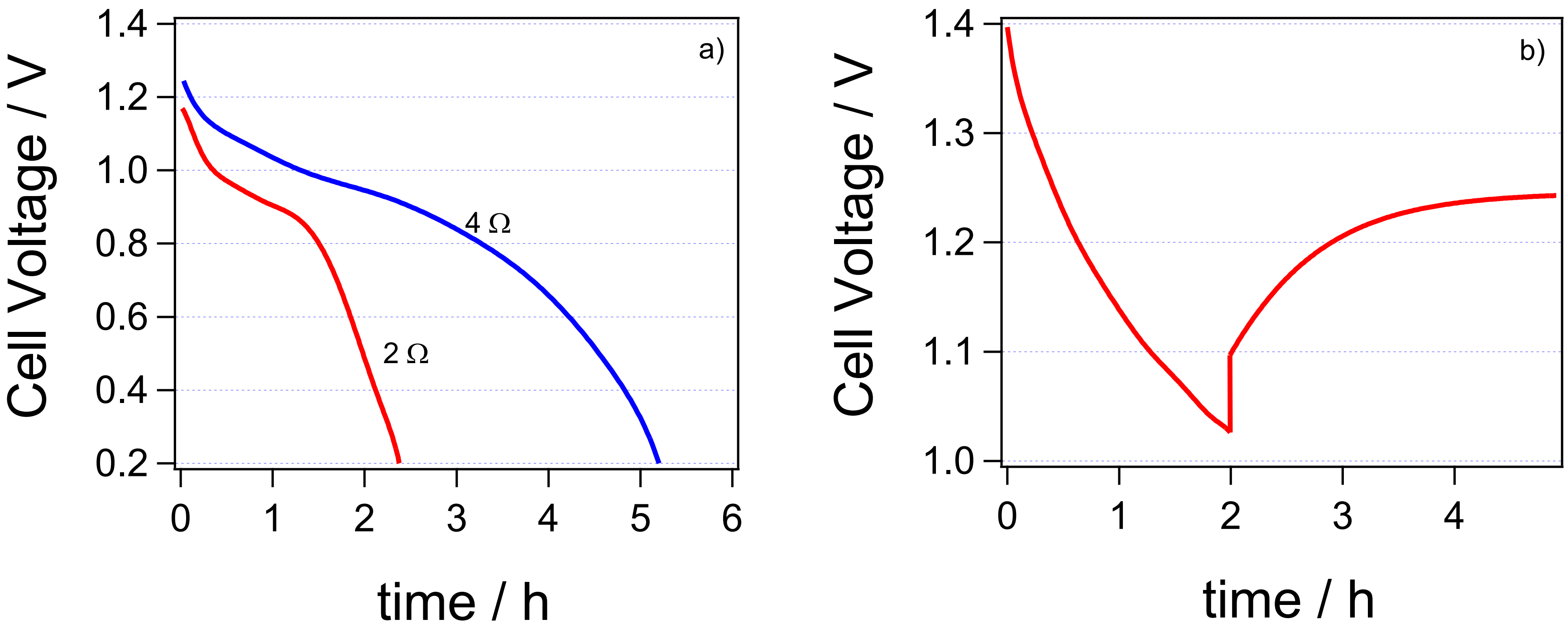
$$H^+_{(surface\ )} \rightarrow H^+_{(bulk\ )}$$

$$xMnO_{2,(s)} + H^+_{(bulk\ )} + e^- \rightarrow (MnO_2)_{x-1}(MnO \cdot OH)_{(s)}$$

Initially, the cathodic product contains a variable amount of trivalent manganese in a homogeneous phase; at higher levels of discharge a new crystalline modification composed solely of MnO·OH is also formed.

These products may react further with zinc ions to form mixed oxides. The composition of the cathodic discharge product is thus seen to vary in a very complex manner as discharge proceeds, and this is responsible for the characteristic fall in OCV with percentage of service life expended.

In addition, the slow diffusion of protons within the solid MnO_2 results in serious polarization of the cell, especially at high currents.

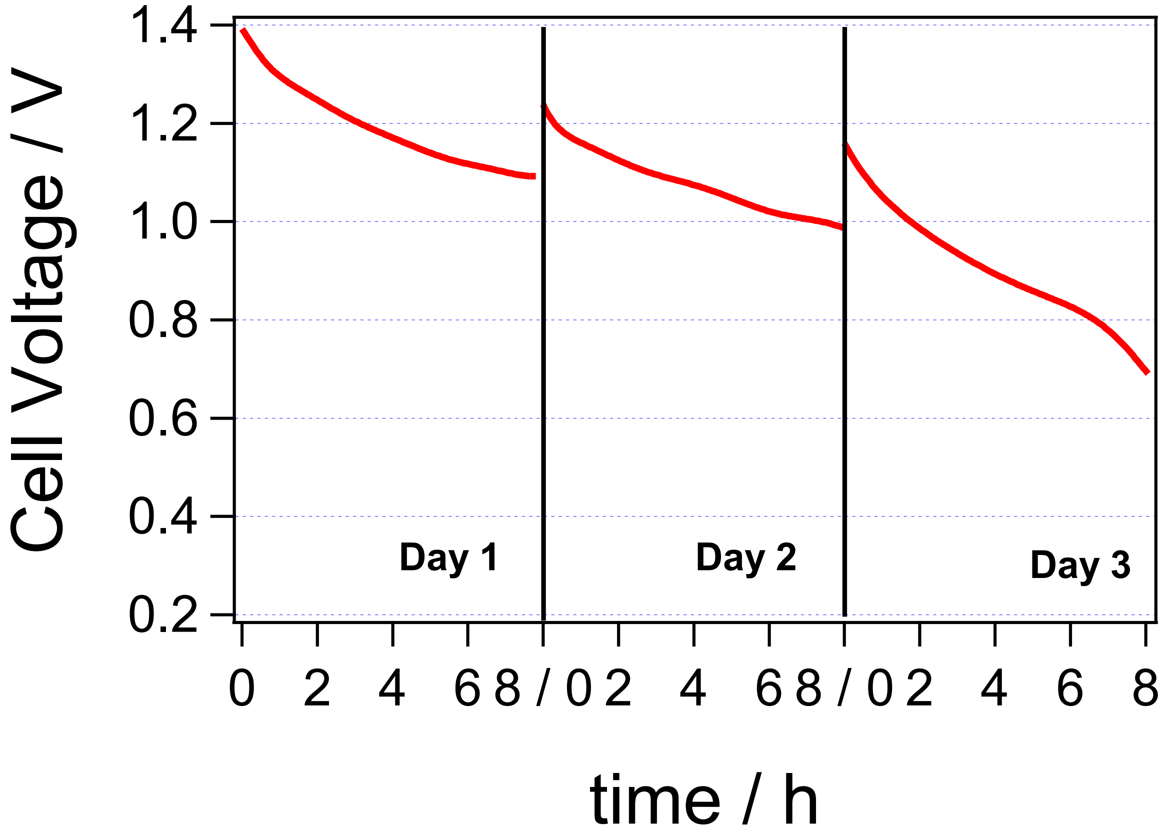


a) Continuous discharge curves of a D-size Leclanché cell through 2 Ω and 4 Ω loads.

b) Recovery of cell voltage after discharge through a 4 Ω load for 2 h.

If the cell is allowed to ‘rest’ for a period while no current is drawn, the cell voltage slowly recovers, as proton diffusion dissipate the high Mn(III) concentration near the surface of the MnO_2 grains and the composition of the solid returns to uniformity (Fig. b) (the recuperation of the cell voltage is also aided by the dispersion of the pH gradient across the cell which also depresses the OCV

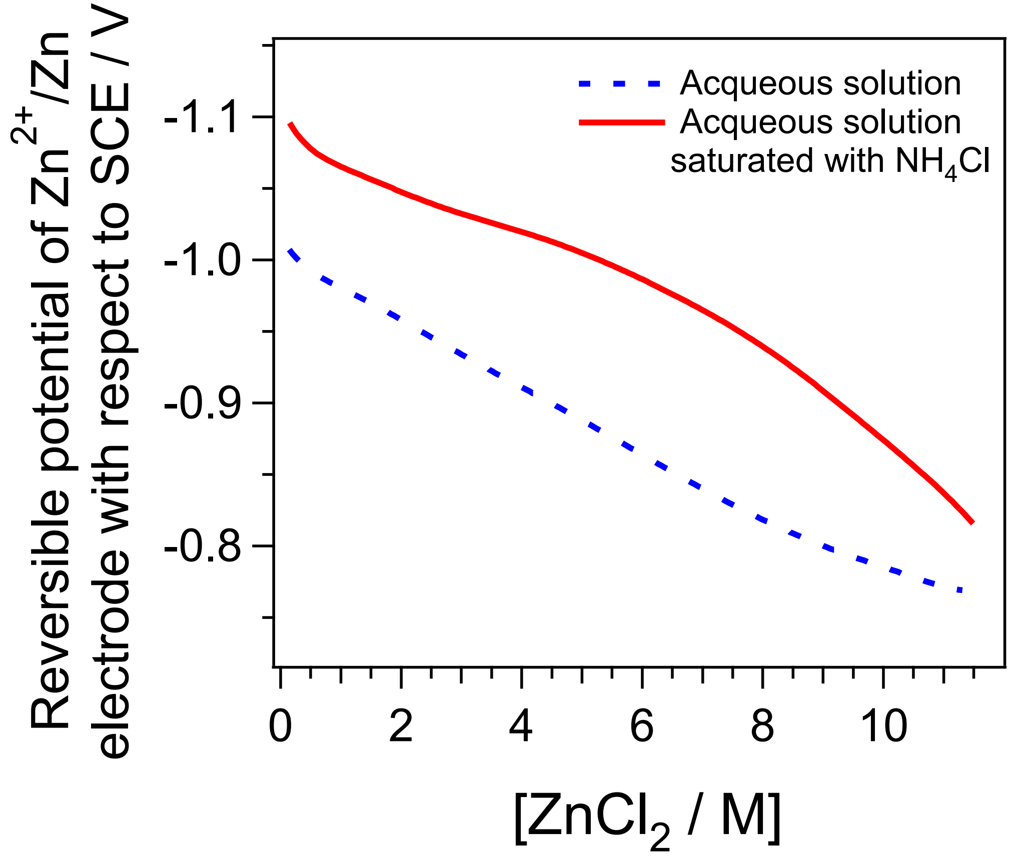
Because of the nature of the cathodic discharge, it can be appreciated that the Leclanché cell must have severe limitations in high current operations. On the other hand in applications requiring intermittent use, the full beneficial effects of the recuperation process may be experienced.



Intermittent discharge curve of a C-size Leclanché cell through a 4 Ω load using an HIF (Heavy Industrial Flashlight) test schedule: 4 min discharge every 15 min over an 8 h period, repeated daily

Anode

In modern cells the anode consists of a zinc alloy sheet, containing small quantities of Pb and Cd to give satisfactory mechanical properties for drawing, extrusion, etc., often lightly amalgamated with mercury. The potential of the zinc electrode with respect to a saturated calomel electrode is shown in Figure as a function of [$ZnCl_2$].

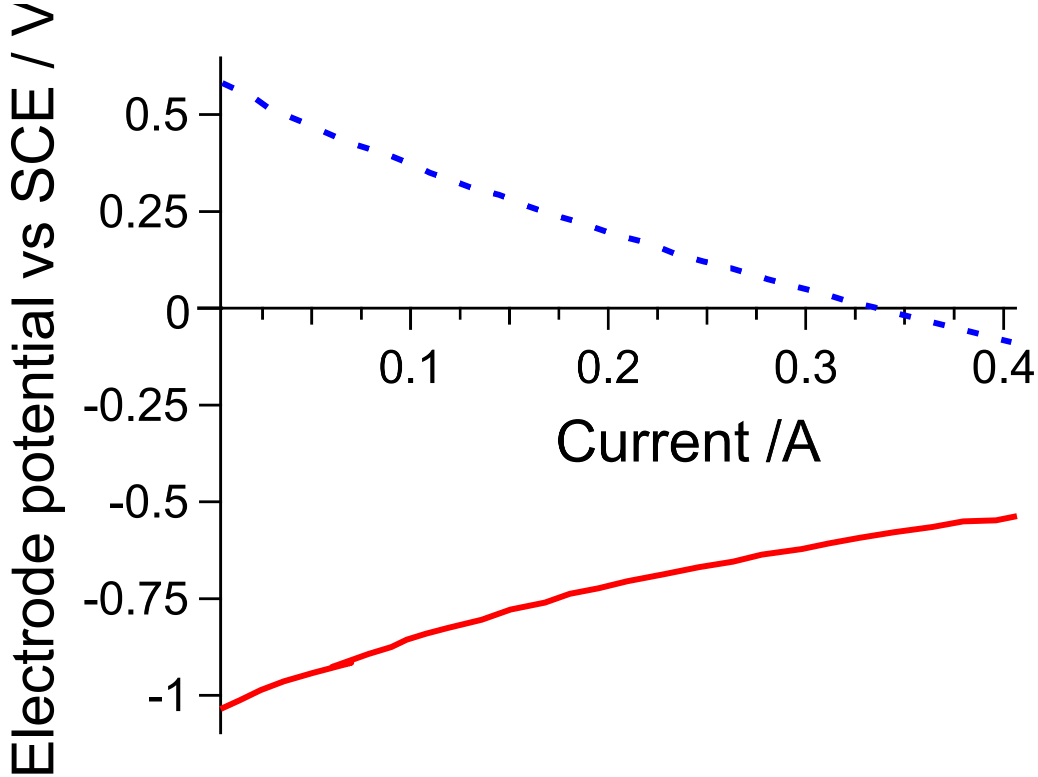


In the presence of NH_4Cl the potential is shifted to more negative values due to the formation of chlorozinc complex (and amminozinc complex at higher pH) with the consequent reduction in the activity of free zinc ions.

Reversible potential of a zinc electrode with respect to a saturated calomel electrode (SCE) as a function of [$ZnCl_2$].

Anode

Electrode polarization of the anode is less severe than that for the cathode, and is mainly concentration polarization resulting from accumulation of $ZnCl_2$ near the electrode surface. During rest periods after discharge, diffusion of $ZnCl_2$ into the bulk of the electrolyte reduces the anode polarization and this also contributes to the recovery of the cell voltage. Polarization behaviour of the cathode and anode of a D-size Leclanché cell is shown.



Polarization curves for anode and cathode of a D-size Leclanché cell: current increased by steps of 25 mA once per minute

Shelf reactions

The most significant self reactions which lead to the deterioration of Leclanché cells are corrosion processes at the anode. These main mechanisms must be considered. First, it oxygen can reach the zinc/solution interface, the reaction

$$Zn_{(s)} + 2NH^{+}_{4,(aq)} + 2Cl^{-}_{(aq)} + \frac{1}{2}O_{2,(g)} \rightarrow Zn(NH_3)_2Cl_{2,(s)} + H_2O_{(l)}$$

become possible.

Effective sealing of the cell is therefore necessary, both to exclude oxygen and to prevent evaporation of water from the electrolyte.

In the absence of the oxygen, a similar corrosion takes place with the evolution of H_2 – despite the reasonably high H overvoltage of Zn:

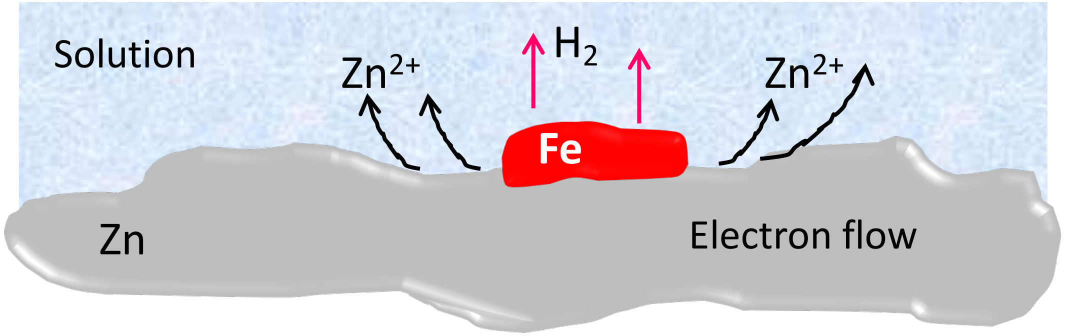
$$Zn_{(s)} + 2NH^{+}_{4,(aq)} + 2Cl^{-}_{(aq)} \rightarrow Zn(NH_3)_2Cl_{2,(s)} + H_{2,(g)}$$

Shelf reactions

This reaction is greatly enhanced if the third corrosion process is widespread, namely displacement reactions which occur when electropositive impurities such as Ni^{2+}, Fe^{2+}, Cu^{2+} etc… are present in the electrolyte, e.g:

$$Zn_{(s)} + Fe^{+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Fe_{(s)}$$

Such displacements result in the formation of local couples where H_2 evolution and Zn dissolution can occur at a greatly accelerated rate. (where the concentration of such impurities is very high, displacement reactions have been known to produce such extensive dendritic growths that the cells have become internally short-circuited.



Mechanism of Zn dissolution by he formation of a local corrosion couple

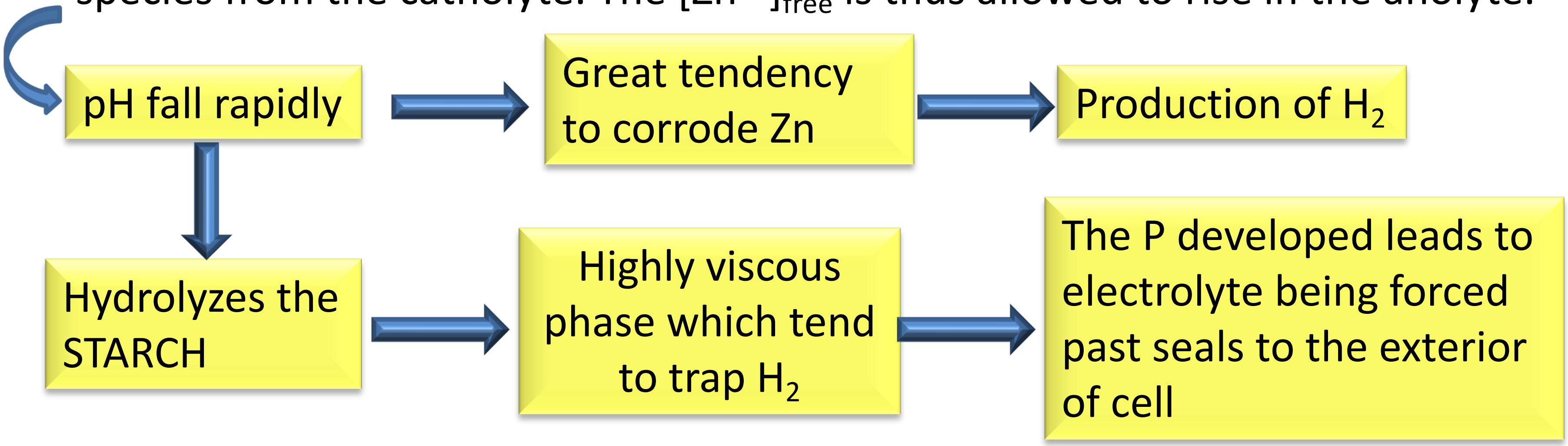
Self reaction - corrosion

- Inhibition of corrosion may be achieved by a number of techniques. If a small quantity of a soluble mercury salt is added to the electrolyte, the zinc surface becomes amalgamated. This increases of electropositive metals, thus preventing the formation of local couples.
- Amalgamation also influences the morphology of the Zn, producing a smoother surface and reducing localized corrosion. While the addition of a Hg salt has been widely adopted by manufacturers of commercial cells, different companies employ a variety of additional corrosion inhibitors ranging from surface active agents, chelating agents to chromates and dichromates. Since the main source of heavy metal impurities is the MnO_2 in the cathode, careful selection or purification of this material is essential.
- Shelf reaxctions at the cathode are of minor importance, although at high T some oxidation of carbon to CO_2 has been reported. Some MnO_2 may also be lost due to reaction with the gelling agent in the electrolyte. While loss from electrolyte by evaporation or reaction to form hydrates may also take place.

Leakage

A longstanding problem of Leclanché dry cells is their propensity to leak after heavy discharge. The origin of this phenomenon may be traced to the formation of insoluble complexes of Zn (involving Cl^-,OH^- and NH_3) in the region between anode and cathode.

The establishment of an insoluble layer drastically reduces diffusion between the two electrode layers, and in particular prevents the transport of basic species from the catholyte. The $[Zn^{2+}]_{free}$ is thus allowed to rise in the anolyte.



pH fall rapidly

Great tendency to corrode Zn

Production of H_2

Hydrolyzes the STARCH

Highly viscous phase which tend to trap H_2

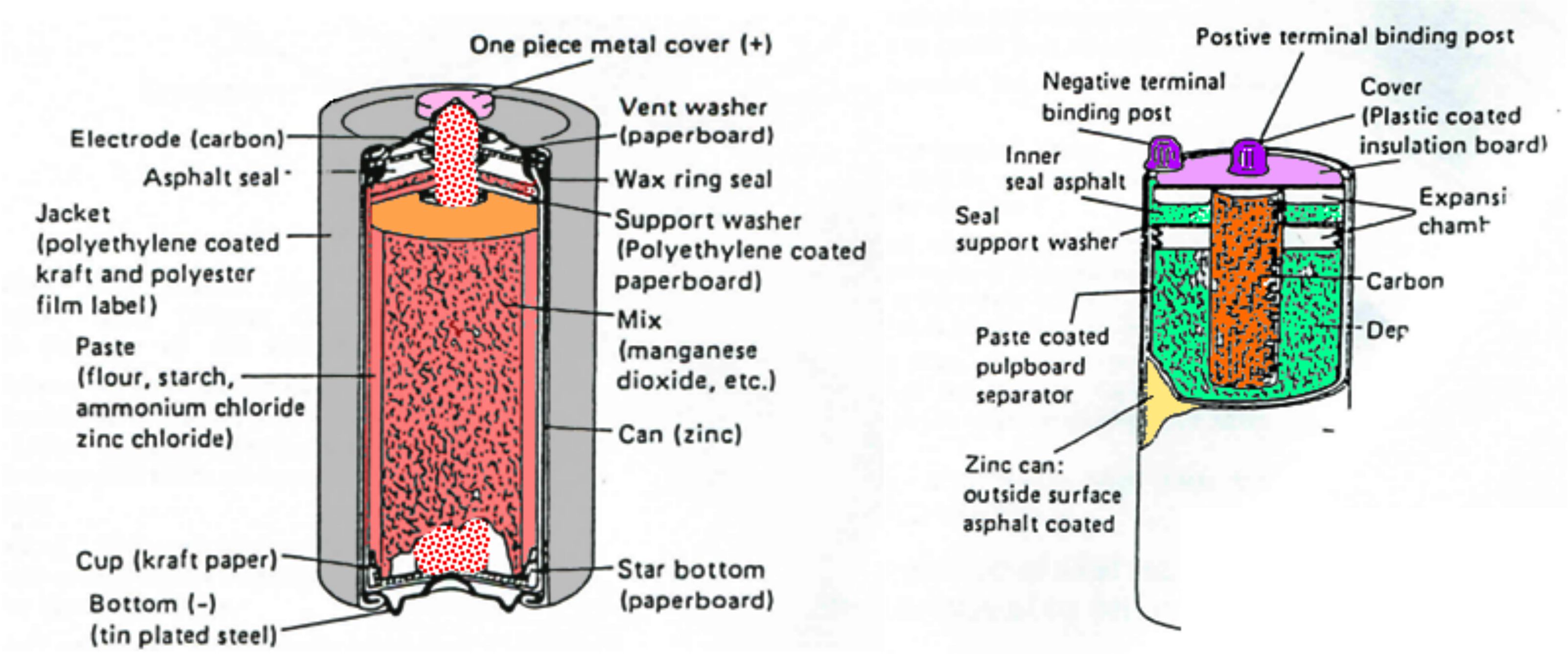
The P developed leads to electrolyte being forced past seals to the exterior of cell

H_2 may also be evolved at the cathode if a cell is left connected to a load after the MnO_2 has all been consumed. Such evolution will continue so long as some Zn remains connected to the load.

Typical power sources

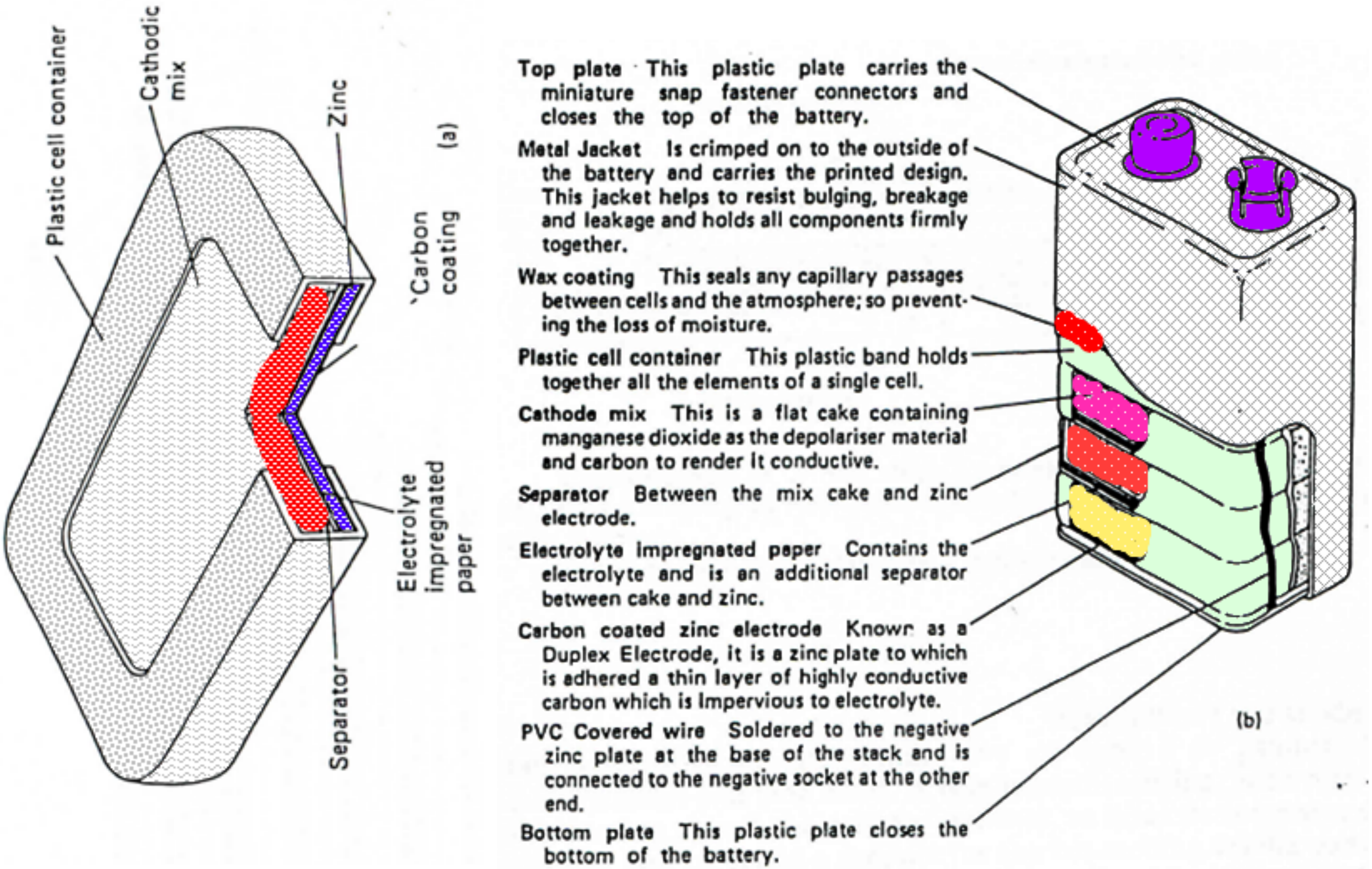
Leclanché cells are manufactured in a range of sizes, from 11.3 mm ∅ x 33 mm high button cells to 66.7 mm ∅ x 166 high alarm cells.

Combination of cells in series and parallel arrangements gives a wide variety of batteries with different capacities and voltages ranging from 1.5 V to 510 V.



Cross-section of a) Standard D-size Leclanché cell and b) high capacity Leclanché alarm cell (by courtesy of Union Carbide)

Typical power sources



Top plate This plastic plate carries the miniature snap fastener connectors and closes the top of the battery.

Metal Jacket Is crimped on to the outside of the battery and carries the printed design. This jacket helps to resist bulging, breakage and leakage and holds all components firmly together.

Wax coating This seals any capillary passages between cells and the atmosphere; so preventing the loss of moisture.

Plastic cell container This plastic band holds together all the elements of a single cell.

Cathode mix This is a flat cake containing manganese dioxide as the depolariser material and carbon to render it conductive.

Separator Between the mix cake and zinc electrode.

Electrolyte impregnated paper Contains the electrolyte and is an additional separator between cake and zinc.

Carbon coated zinc electrode Known as a Duplex Electrode, it is a zinc plate to which is adhered a thin layer of highly conductive carbon which is impervious to electrolyte.

PVC Covered wire Soldered to the negative zinc plate at the base of the stack and is connected to the negative socket at the other end.

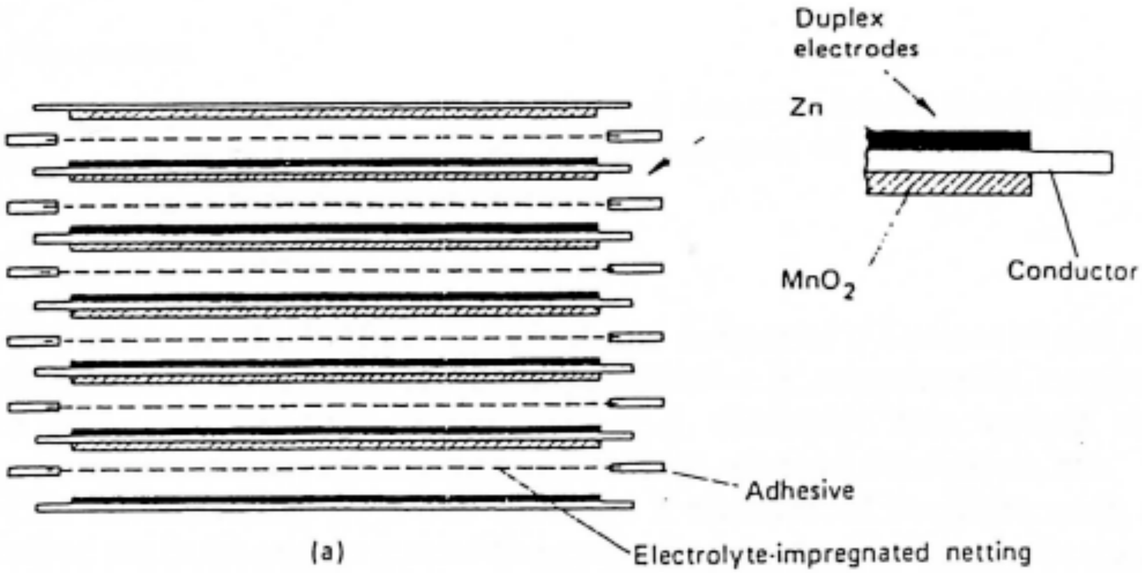
Bottom plate This plastic plate closes the bottom of the battery.

Cross section of a) a flat Leclanché cell and b) 9V battery of 6 flat Leclanché cells (by courtesy of Berec)

Typical power sources

The electrolyte/separator usually consists of one or two layers of different electrolyte impregnated papers which have been treated with suitable gelling agents. The cathode mix of MnO_2, acetylene black and electrolyte is formed into a flat cake and each cell is held together by a plastic band, as shown. The group of six cells are sealed with a wax coating and assembled within a metal jacked. No provision of expansion volume is found necessary with this form of construction, and a relatively high energy to volume ratio is realized.

Typical power sources

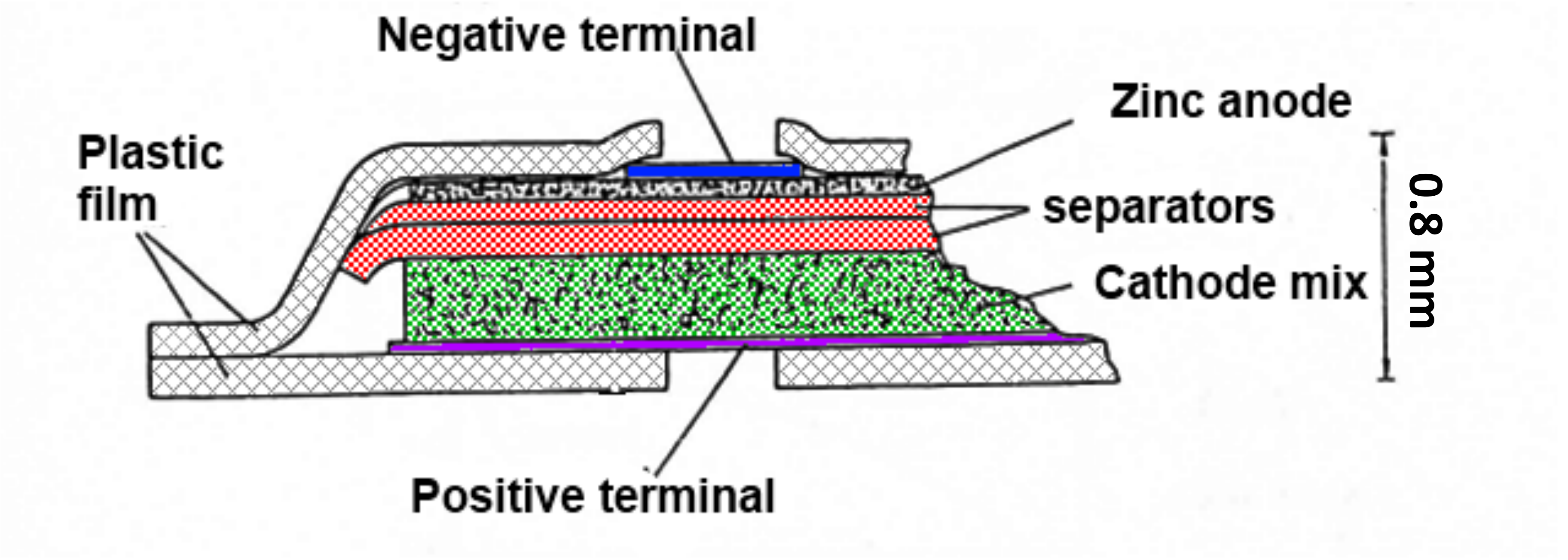


a) Cross-section of 3 mm thick Leclanché battery used in automatic cameras after a drawing by Ray-o-Vac.

b) a detail of the construction of the duplex electrodes is shown.

Both cathode and anode mixes contain a water-based latex binder and are applied or 'painted' onto a conductive sheet and then dried. A thin synthetic netting, just over 0.1 mm thick used to absorb the gelled electrolyte, to separate successive duplex electrodes, and to act as a support for the hot-melting sealing compound applied around its perimeter. This advanced technology battery containing 4 cells has a cross-sectional area of 7.0 x 8.5 cm and a thickness of less than 3 mm. it weight about 19 g.

Typical power sources



Cross section of the Matsushita 'paper battery'

Another slim Leclanché cell is the 'Paper Battery' produced by Matsushita. This 1.5 V cell is manufactured in a number of different shapes and has a maximum thickness of 0.8 mm. a circular cell with a diameter of 38 mm weight 1.5g.

Performance

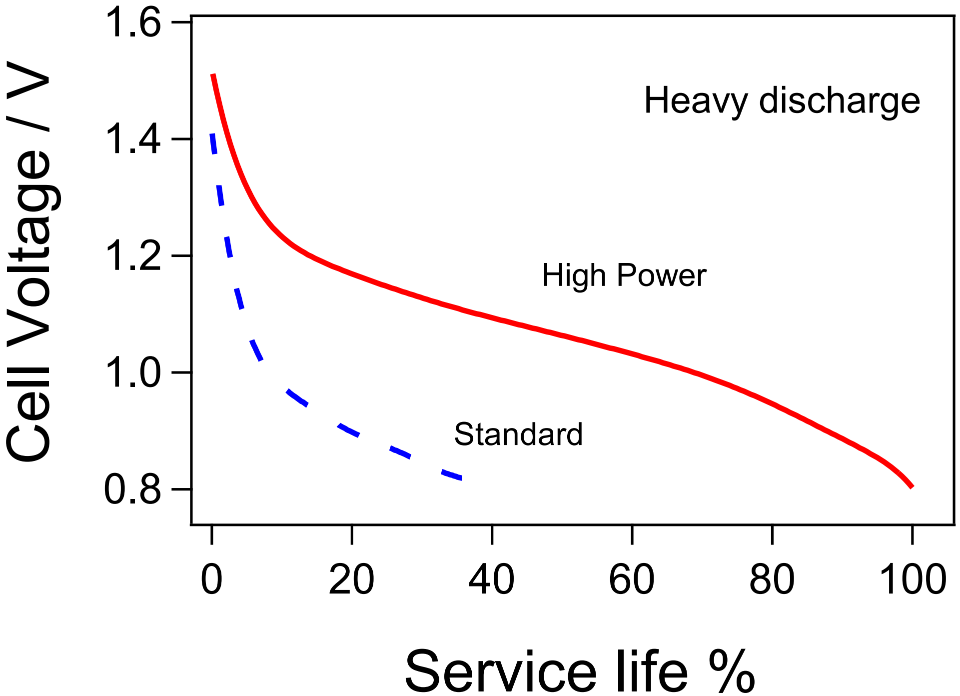
The practical capacity of a Leclanché cell does not have a fixed value since it varies according to the pattern and conditions of discharge – to a much greater extent than for most other cells.

The factor which affect the electrical output may be divided into two groups:

i) Cell dependent, e.g. construction, composition and size

ii) User dependent, e.g. discharge rate, cut-off voltage. Operating schedule, operating T, storage conditions, etc…

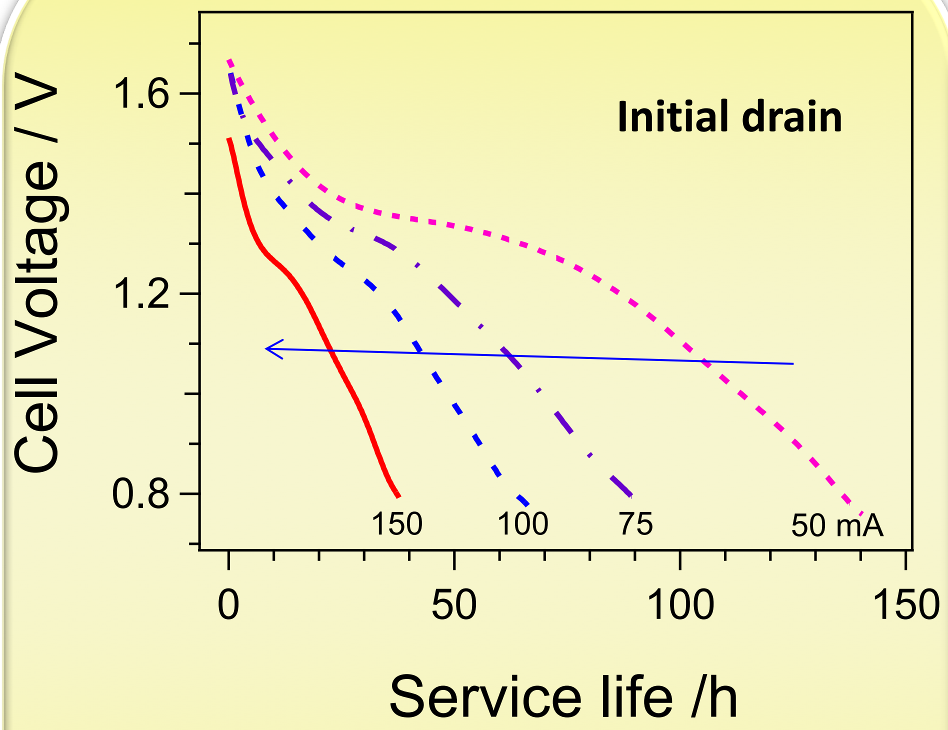
The construction of a cell involves a number of variables, such as the relative amount and nature of cathodic mix, type of separator used, etc…



Difference in service life of standard and 'high power' Leclanché D-size cells discharged for 30 min per day through 2 Ω loads

Performance

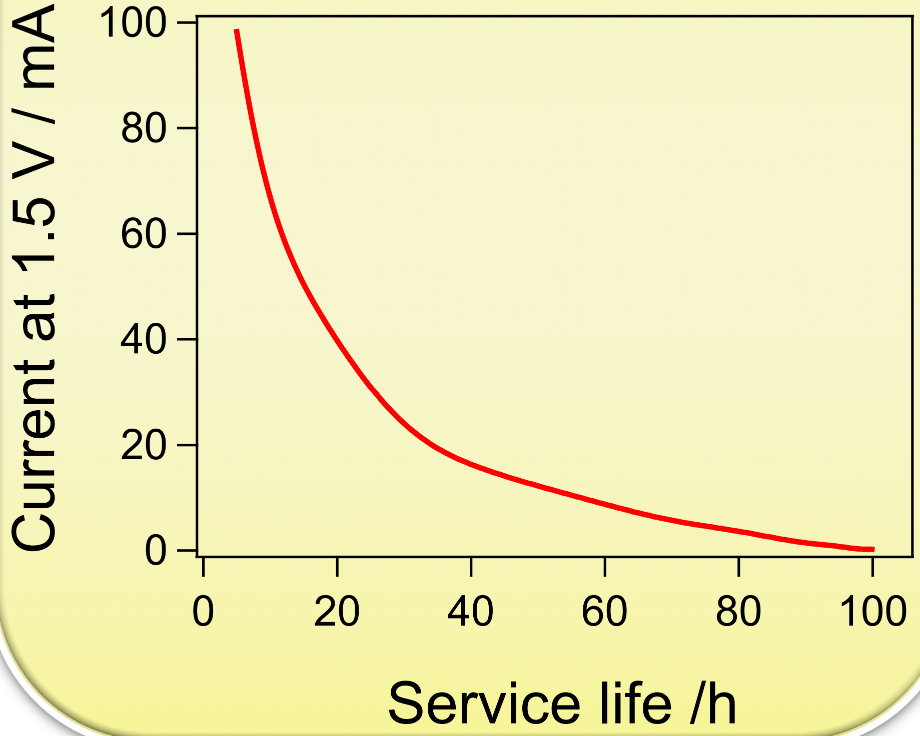
For a similar construction and composition, and a fixed duty schedule, higher capacities are obviously obtained by using cells of larger size.



Effect of discharge rate on service of D-size Leclanché cells discharged at 2 h per day

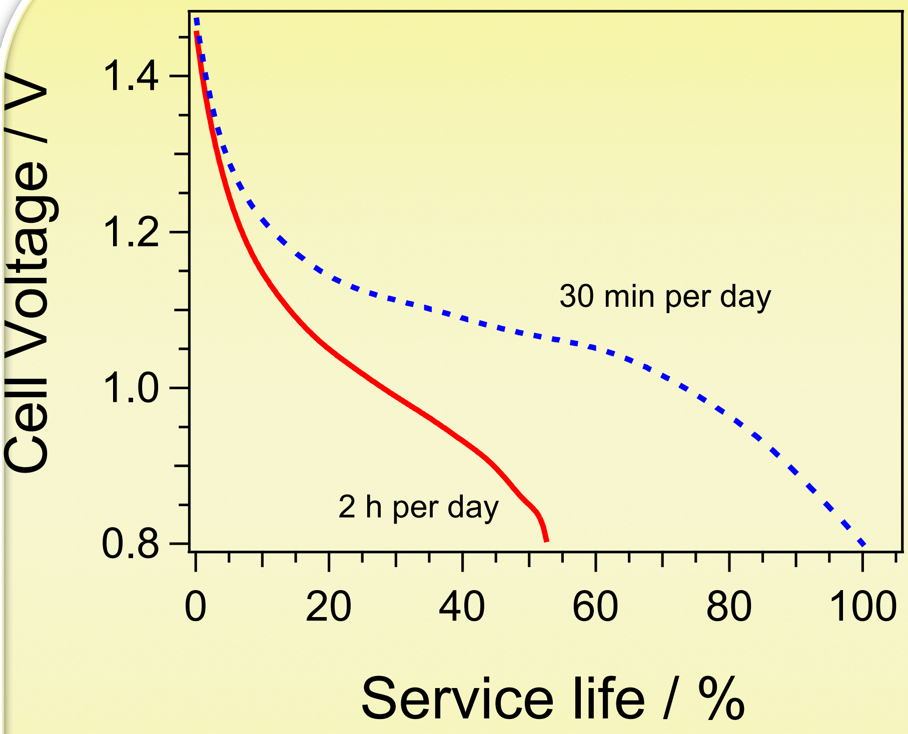
Effect on service life of initial current drain.

D-size Leclanché cell discharged at 4 h per day or to 0.9 V cut-off.

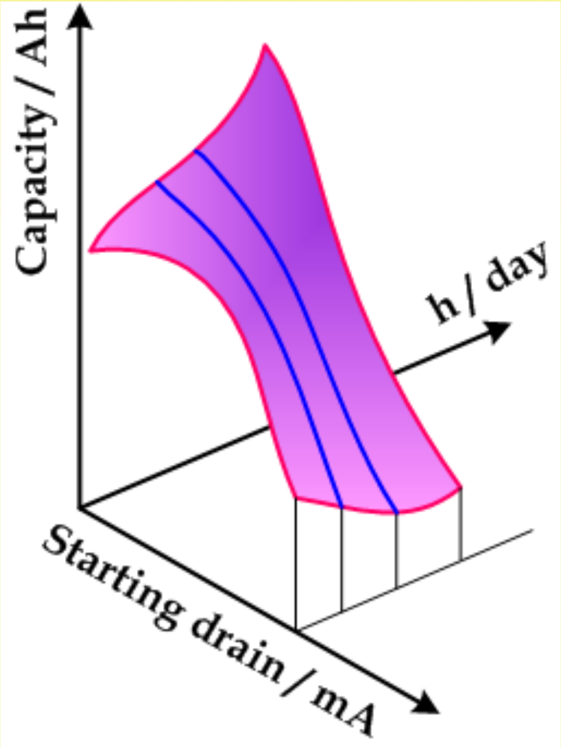


Performance

Unless the current drain is very low, Leclanché cells give a much better performance when used on an intermittent basis.

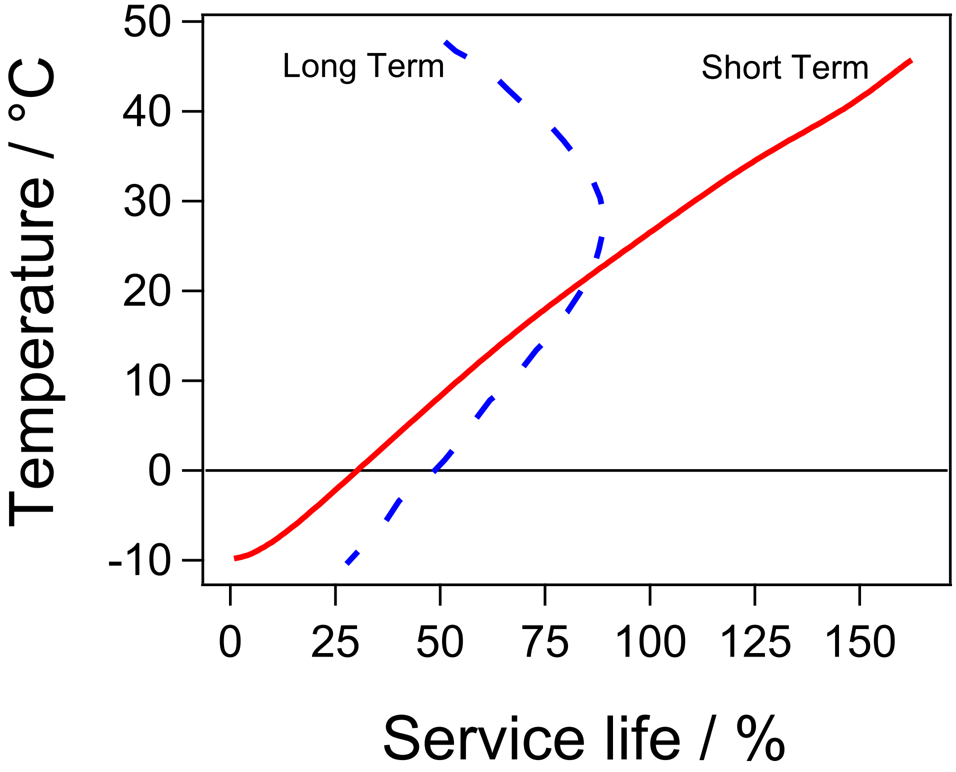


Effect of operating schedule on service life of a standard D-size Leclanché cell discharged through a 5 Ω load.



Capacity of D-size standard Leclanché cells as a function of duty cycle and initial current drain (by courtesy of Union Carbide)

Performance



Other factors which affect the electrical output are the operating T and the storage conditions. Cells are generally tested at 21°C. Higher T increase the energy output but reduce the shelf-life.

Effect of T on the service life of a 9V Leclanché flat battery subjected to short term (≈6 month) discharge (by courtesy of Berec)

The low T behaviour of normal Leclanché cells is very poor. Special Leclanché cell with altered electrolytes have been used in the past for low temperature applications, but in current practice such cells are replaced by Li, $ZnCl_2$ or Zn/alkaline MnO_2 cells which have greatly superior low T behaviour.

Performance

T / °C	Normalized capacity	
	Leclanché	$ZnCl_2$
37.8	1.40	1.15
26.7	1.10	1.05
21.1	1.00	1.00
15.6	0.90	0.95
4.4	0.70	0.85
-6.7	0.45	0.70
-17.8	0.25	0.45

Effect of T on he capacity of D-size Leclanché and $ZnCl_2$ cells when discharged continuously through 2.25 Ω to a cut-off voltage of 0.9 V

Advances in Leclanché dry cell performance have been continuous since the time of Geinessner.

Between 1900 and 1960 the specific capacity of cells double roughly every 20 years. Between 1960 and 1980 a further increase in capacity of over 50% has been achieved.

Despite the rapid evolution of new forms of primary battery in recent years, the hold of the Leclanché cell on the market remains very strong for those applications for which its relatively poor discharge characteristic are adequate. The reasons for this are not hard to find: the materials used in its construction are readily available and relatively cheap, while fabrication processes are comparatively straightforward.

Zinc Chloride Cells

The so-called ‘zinc chloride cells’ are basically Leclanché cells in which the ammonium chloride has been completely replaced by $ZnCl_2$. The resulting cells have a better service capacity at high current drain, at low T, and on continuous discharge.

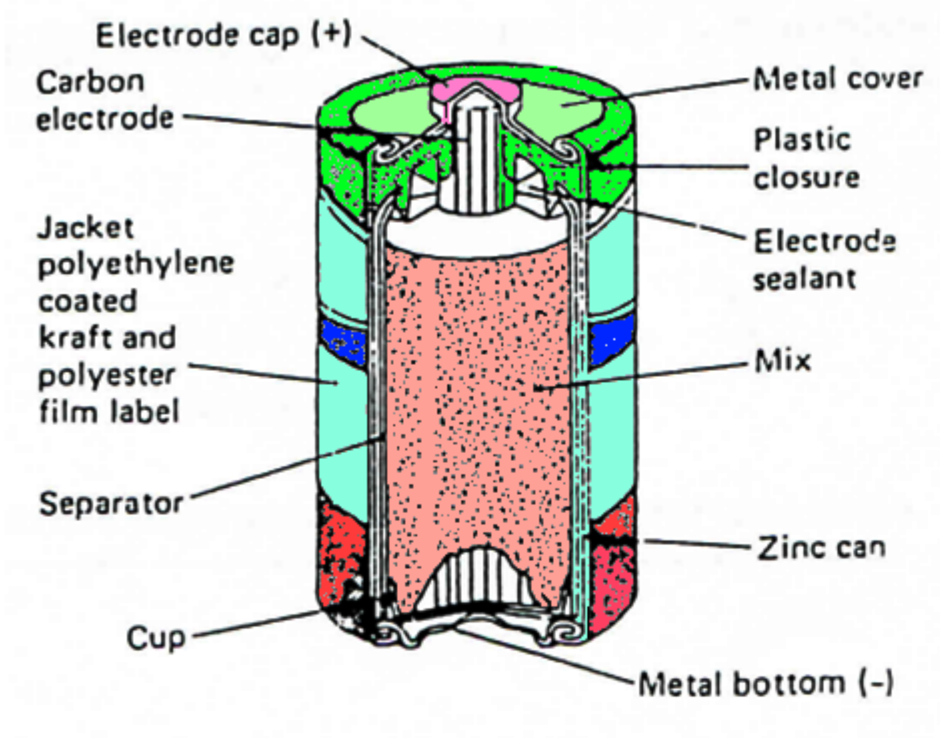
The cell may be written as: $Zn_{(s)}\left|ZnCl_{2,(aq)}\right|MnO_{2,(s)}, C_{(s)}$

and the OCV is again about 1.5 V. The accepted overall cell reaction is

$$4Zn_{(s)} + ZnCl_{2,(aq)} + 8MnO_{2,(s)} + 8H_2O \\ \rightarrow 8MnO \cdot OH_{(s)} + ZnCl_2 \cdot 4Zn(OH)_{2,(s)}$$

It should be noted that water is consumed in the cell reaction so that there is a tendency for the cell to dry out during discharge. The anode and cathode are similar to those in the Leclanché cell although higher quality MnO_2 and a higher percentage of acetylene black are normally used. The advantages of this system arise from the properties of the electrolyte where higher rates of diffusion are possible, since there is less tendency for the electrolyte layers near the electrode surfaces to be blocked by insoluble products.

Zinc Chloride Cells



The range of operating T is much wide so that this system can form satisfactory low temperature power supply.

Further, higher current densities may be obtained without unacceptable polarization: for this reason some manufacturers refer to $ZnCl_2$ cells as ‘Heavy Duty’ batteries.

Cross-section of a D-size $ZnCl_2$ cell. (by courtesy of Union Carbide)

In the $ZnCl_2$ a more sophisticated sealing system is generally employed since prevention of leakage is more important with the more acid electrolyte. $ZnCL_2$ cells always use a thin treated paper separator.

The improved performance of the $ZnCl_2$ cell is offset by the higher cost incurred through using a better quality cathode mix and more complex fabrication due to the requirement of more reliable seals.

Alkaline manganese cells

This type of cell is another variant on the basic Leclanché cell. In this case the electrolyte is a concentrated aqueous solution of KOH (about 30%), partly converted to potassium zincate by the addition of ZnO. The main advantage of alkaline manganese cells over Leclanché cells is their relatively **constant capacity over a wide range of current drains and under severe service schedule conditions**.

Another feature of this system is that it can be basis of a secondary battery system. The cell reaction may be written formally as:

$$2Zn_{(s)} + 2MnO_{2,(s)} + H_2O \rightarrow 2MnO \cdot OH_{(s)} + 2ZnO_{(s)}$$

But is in practice much more complex than this due to further reduction of the manganese, as discussed below, and the formation of various soluble zincate species.

The OCV is 1.55 V at room temperature.

Alkaline manganese cells

ELECTROLYTE

A variable quantity of ZnO is added to the concentrated KOH solution, depending on the system characteristics required. The electrolyte is immobilized using carboxymethylcellulose and a non-woven fabric separator made of natural or synthetic fibers resistant to the high pH is placed between the electrode.

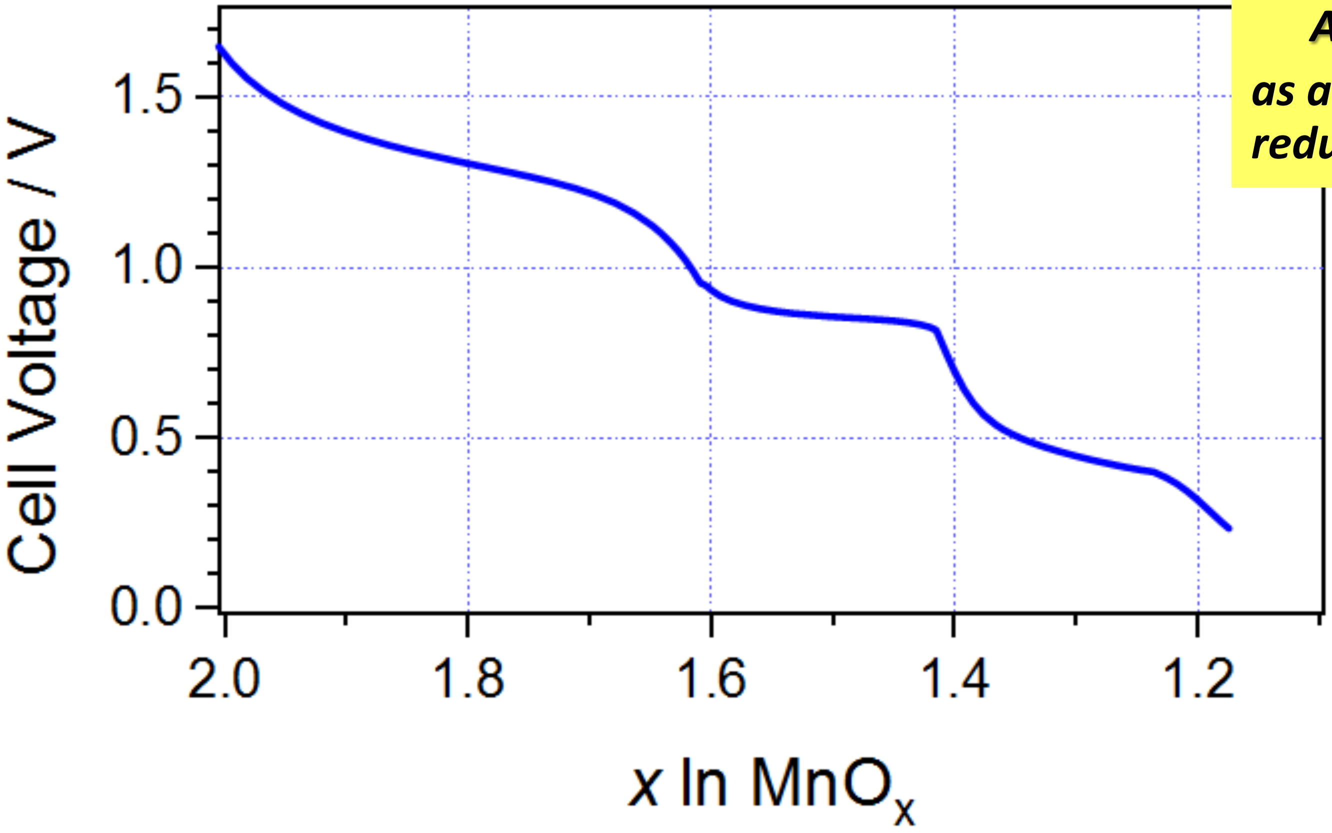
CATHODE

The cathode mix is a compressed mixture of electrolytic MnO_2 and graphite in a ratio of 4-5:1, wetted with electrolyte. The cathode current collector is generally the external steel can. Reduction of MnO_2 in alkaline conditions is a complex process and follows a number of steps which can be written formally as:

$$MnO_2 \rightarrow MnO_{1.5}$$
$$MnO_{1.5} \rightarrow MnO_{1.33}$$
$$MnO_{1.33} \rightarrow MnO$$

The last two stages are only possible at very low current drain.

Alkaline manganese cells

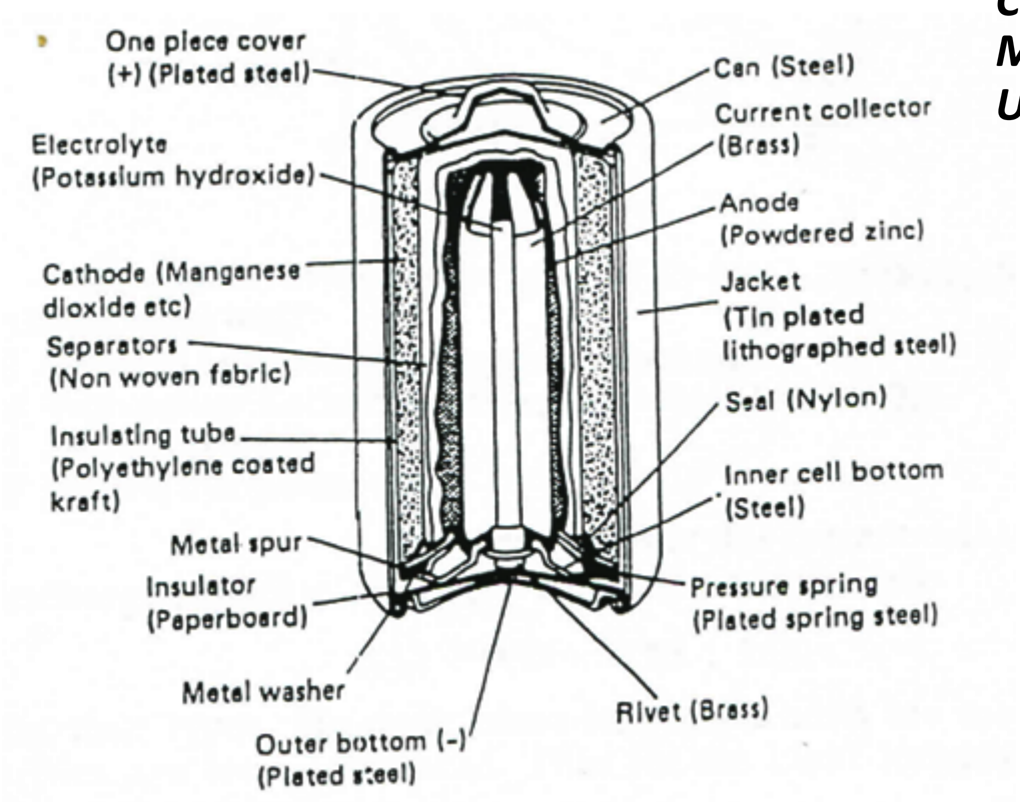


Cell voltage of an
Alkaline Manganese Cell
as a function of the degree of reduction of MnO_2

Provided that the reduction does not exceed a level equivalent to MnO1.33 the reaction can be reversed and the cathode main discussion of secondary aqueous system follows the secondary alkaline manganese cell is so similar to the primary cell that it is more convenient to consider it here

Alkaline manganese cells

ANODE



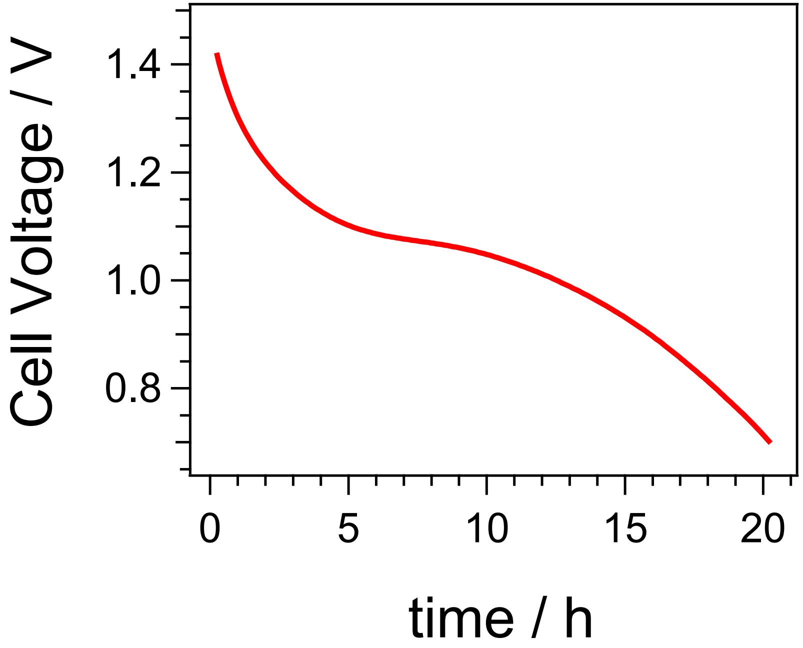
Cross-section of D-size alkaline Manganese primary cell (by courtesy of Union Carbide)

The anode is a hollow cylinder of powdered amalgamated zinc set in a carboxymethylcellulose gel. The current collector is usually made of brass and the interior space is filled with immobilized KOH solution.

Alkaline manganese cells

PERFORMANCE

The discharge curve for a D-size alkaline manganese cell with an initial current drain of 500 mA is shown. Compared with even the best Leclanché cell of this size, the alkaline manganese cell has a capacity advantage of at least a factor 4 in high current continuous discharge applications.

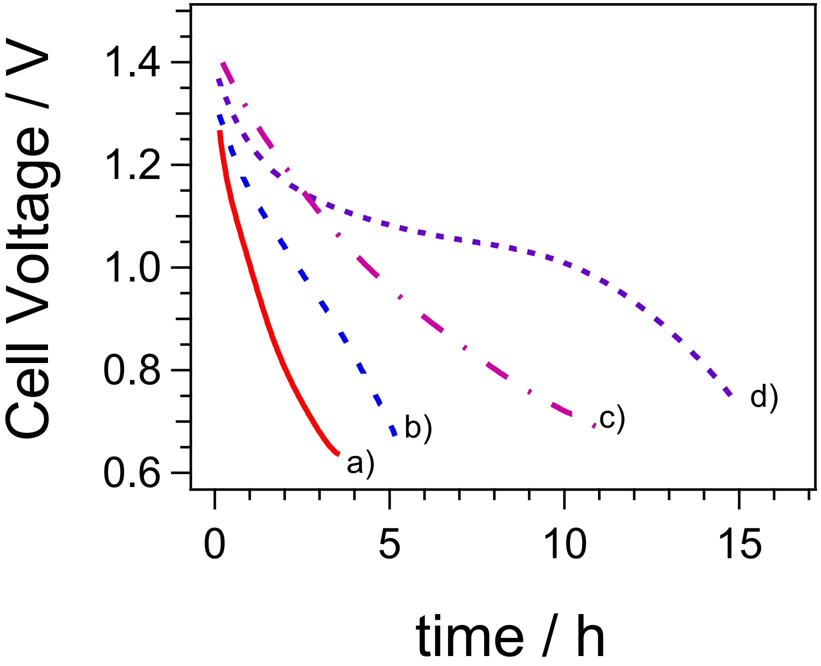


Discharge curve of a D-size alkaline manganese primary cell with an initial current drain of 500 mA.

The shelf life of these cells is also good: after four year storage at 21°C they retain more than 80% of their initial capacity. At low T, especially at low current drain, the performance is as good as that of the $ZnCl_2$ cell.

Alkaline manganese cells find applications in devices such as electric shavers, radio-controlled models (motive power and glo-plug ignition), portable tape cassette players, emergency lighting, etc…

Alkaline manganese cells



Comparison of the performances of Zn-MnO_2 primary systems under 2.25 Ohm continuous test:

- ***a)*** ***Standard Leclanché cell based on natural ore***
- ***b)*** ***'high power' Leclanché cell based on electrolytic MnO_2***
- ***c)*** ***$ZnCl_2$ cell***
- ***d)*** ***Alkaline manganese cell***

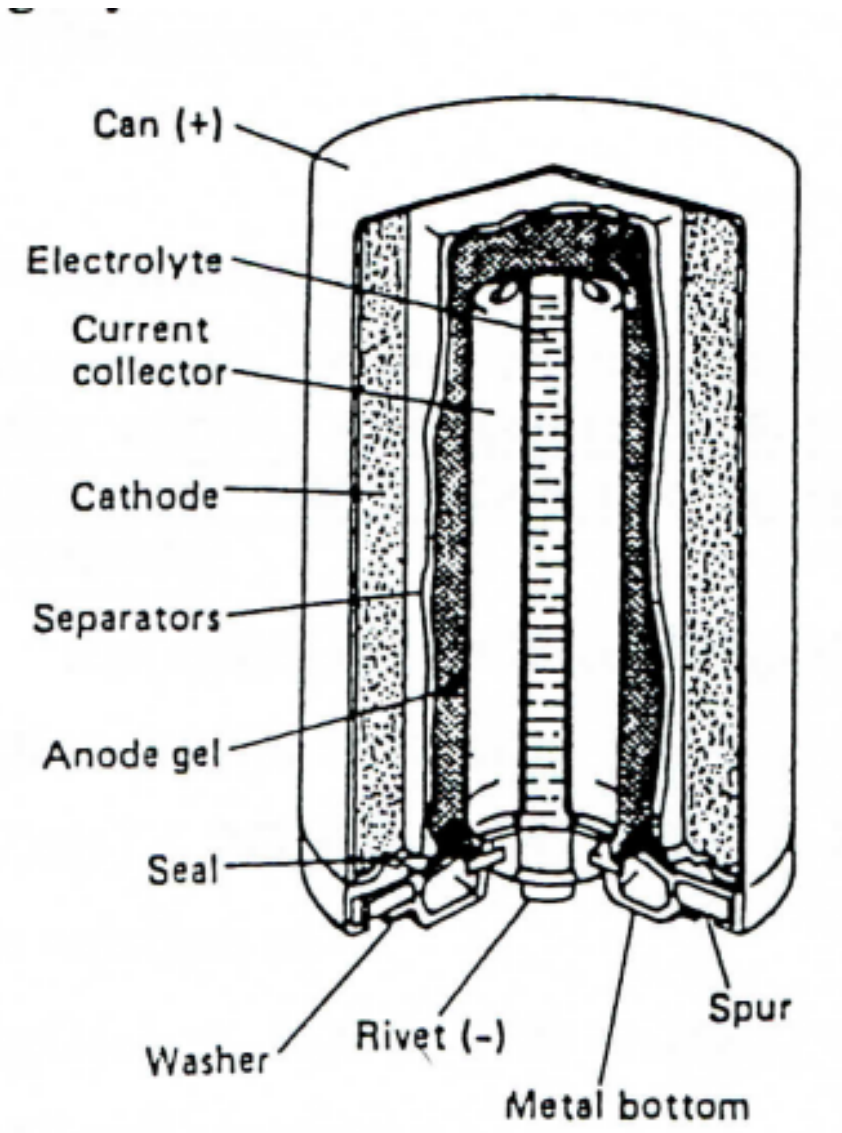
The difference at this current drain are striking: the discharge capacity with a 0.9 V cut-off are in the ratio

0.12 : 0.24 : 0.55 : 1.00

For the four type. However when less severe tests are considered, the disparities are less pronounced. Thus for the Light Industrial Flashlight (LIF) test, the ratio are

0.40 : 0.61 : 0.86 : 1.00

Alkaline manganese cells



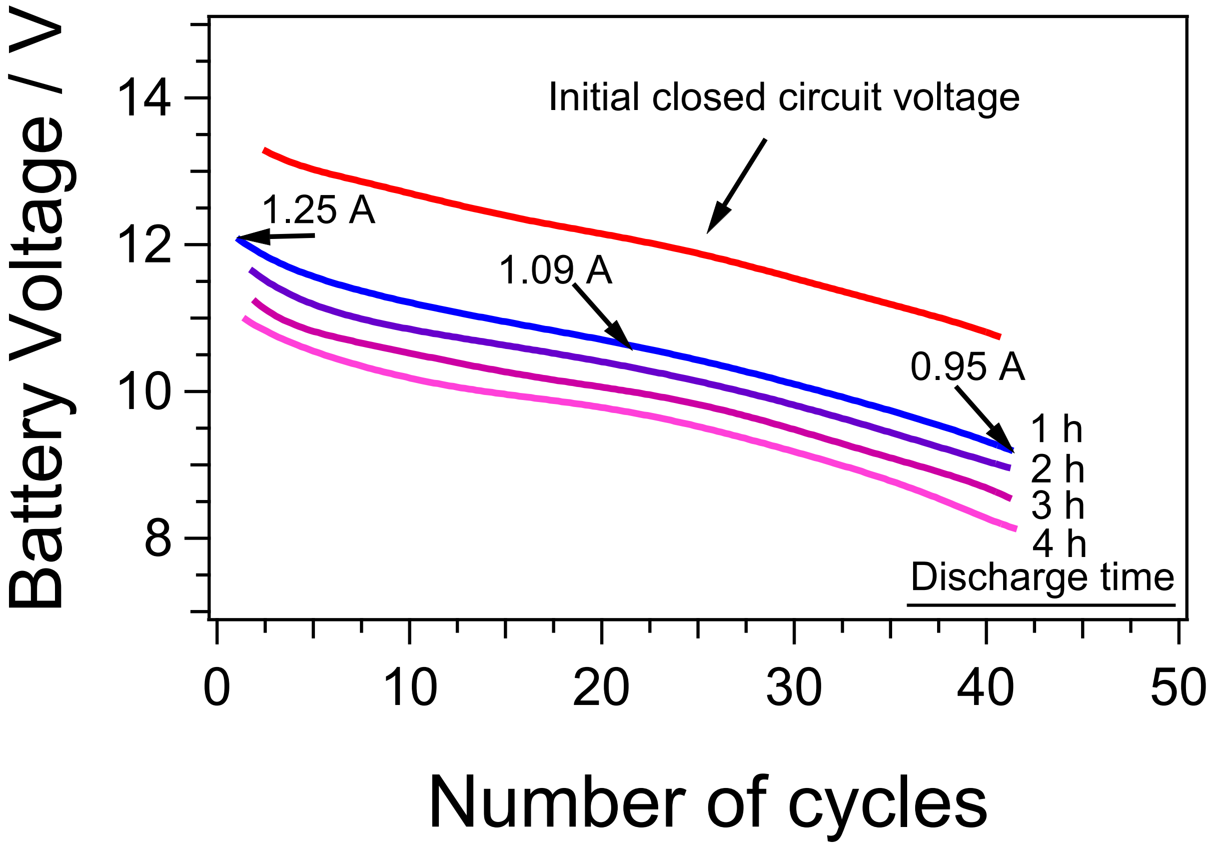
Alkaline manganese secondary cells are also sealed units.

The most important modification in the thicker separator required to prevent short circuits due to dendritic growth of zinc during recharge.

In addition, the cathode mix contains extra binding agents to help preserve its integrity when volume changes occurs during charge/discharge cycles.

Cross-section of a D-size alkaline manganese secondary cell. (by courtesy of Union Carbide)

Alkaline manganese cells



Performance of a 15 V alkaline manganese secondary battery as a function of the charge/discharge cycle. Charge: 16 h voltage limited taper; discharge 4 h through 9.6 Ω

The initial discharge characteristics of the secondary cells are very similar to those of the primary system. However the cell voltage, and hence the available power and energy declines as the cycle life of the system runs its course.

With this type of secondary cell, the cut-off voltages for both discharge and charge are critical.

Alkaline manganese cells

ON DISCHARGE THE CELL VOLTAGE SHOULD

Not fall below 0.9 V, since otherwise irreversible reduction of the cathode below the nominal MnO1.33 may occur. Overcharge has also to be avoided since no provision is made for it, and the use of voltage-limited taper current charging is recommended.

Rechargeable alkaline manganese batteries are used in applications where low initial cost is important.

The number of cycles obtainable under similar operating conditions is considerable less than for, say, nickel-cadmium batteries, but the cost is much lower.

Commercially, this system has had little success.

The Zinc – Mercury oxide system

This system, commonly known as the ‘mercury cell’, is based on an amalgamated zinc anode, a concentrated aqueous KOH electrolyte – saturated with zincate ion by ZnO, and a HgO/C cathode:

$$Zn_{(s)}\left|ZnO_{(s)}\right|KOH_{(aq)}|HgO_{(s)},C_{(s)}$$

The anode reaction may be written as

$$Zn_{(s)}+2OH^{-}_{(aq)}\rightarrow ZnO_{(s)}+H_2O_{(l)}+2e^{-}$$

and the cathode reaction as

$$HgO_{(s)}+H_2O_{(l)}+2e^{-}\rightarrow Hg_{(l)}+2OH^{-}_{(aq)}$$

So that the overall cell reaction is

$$HgO_{(s)}+Zn_{(s)}\rightarrow Hg_{(l)}+ZnO_{(s)}$$

The Zinc – Mercury oxide system

Two important points to note are:

a) The invariance of the electrolyte solution;

b) The constancy of the chemical potentials of reactants and products, as the discharge proceeds

One consequence of the effective non-involvement of the electrolyte is that only a very small quantity is required in a working cell. Another is a relatively constant internal resistance, leading to a flat discharge curve. The constancy of chemical potentials implies a constant OCV during the course of discharge.

	Free energy / kJ mol^{-1}
$HgO_{(s)}$	58.4*
$ZnO_{(s)}$	318.2*
Cell reaction	258.8

*** Data from Latimer's 'Oxidation Potentials'***

cell e.m.f. is 1.347 V

Agreement with the OCV of 1.357 V of commercially produced cell.

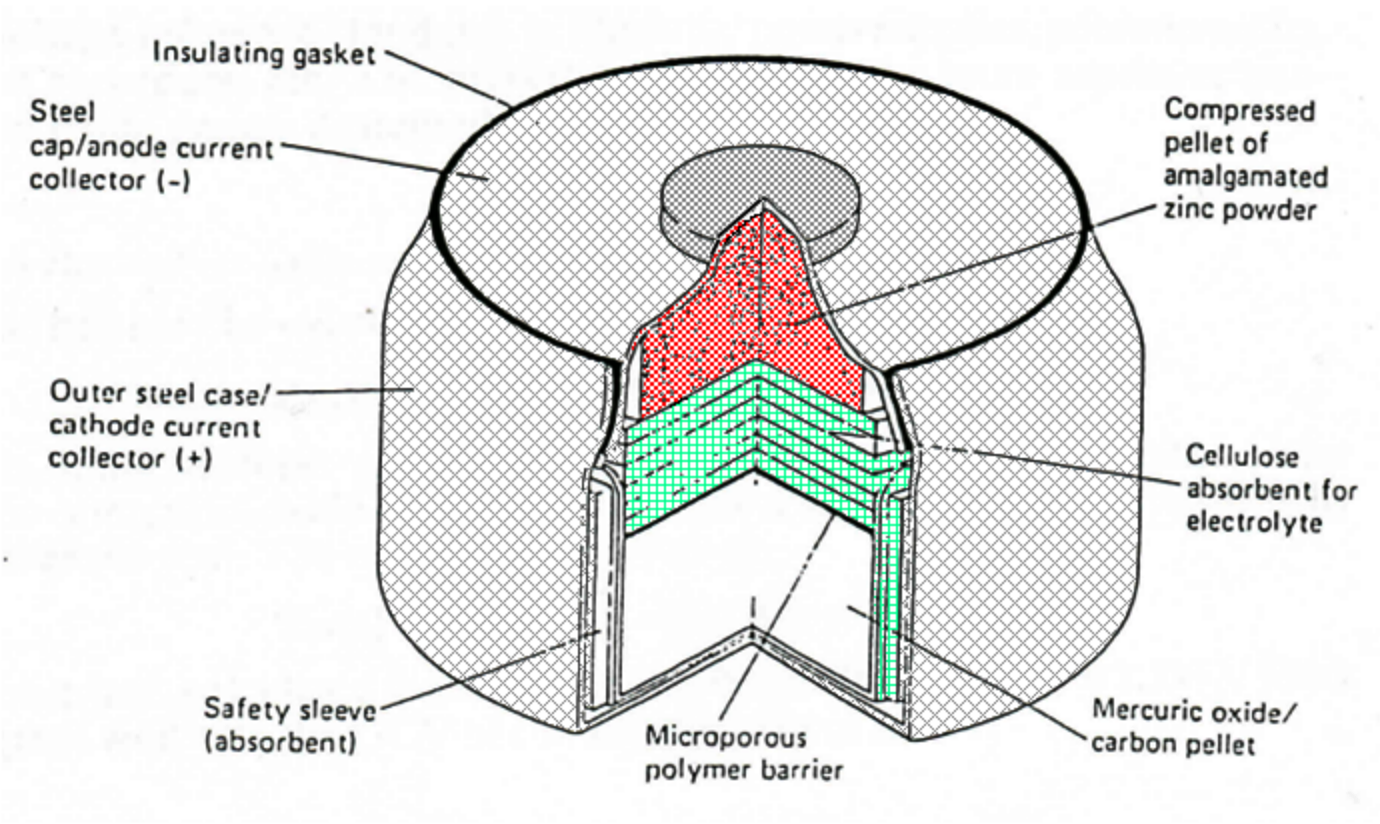
The OCV may be slightly increased by adding MnO_2 to the cathode mix.

The Zinc – Mercury oxide system

The electrolyte is usually an approximately **40% KOH solution saturated with ZnO**, to which corrosion inhibitors have been added. The KOH is occasionally replaced by NaOH. Caustic soda solution have a lower tendency to creep, but have a higher electrical resistance. **The electrolyte is immobilized using felted cellulose**. The most common anode is a **porous compressed cylindrical pellet of amalgamated zinc powder and electrolyte** (possibly gelled). An alternative configuration is the ‘wound anode’ usually found in secondary zinc-mercury oxide cell, which uses a spiral of corrugated zinc foil interleaved with an absorbent paper strip.

The cathode pellet consists of **HgO together with 5-10% of finely divided graphite**, added to increase the electronic conductivity and to minimize the coalescence of mercury formed during discharge. The cathode has always a larger capacity than the anode. The cell is therefore ‘zinc limited’: i.e. in an exhausted cell there is no zinc left which might corrode and thus leas to H2 pressure developing in the cell. A microporous plastic barrier layer is generally placed next to the cathode pellet to prevent internal short circuits caused by the displacement of free mercury on graphite.

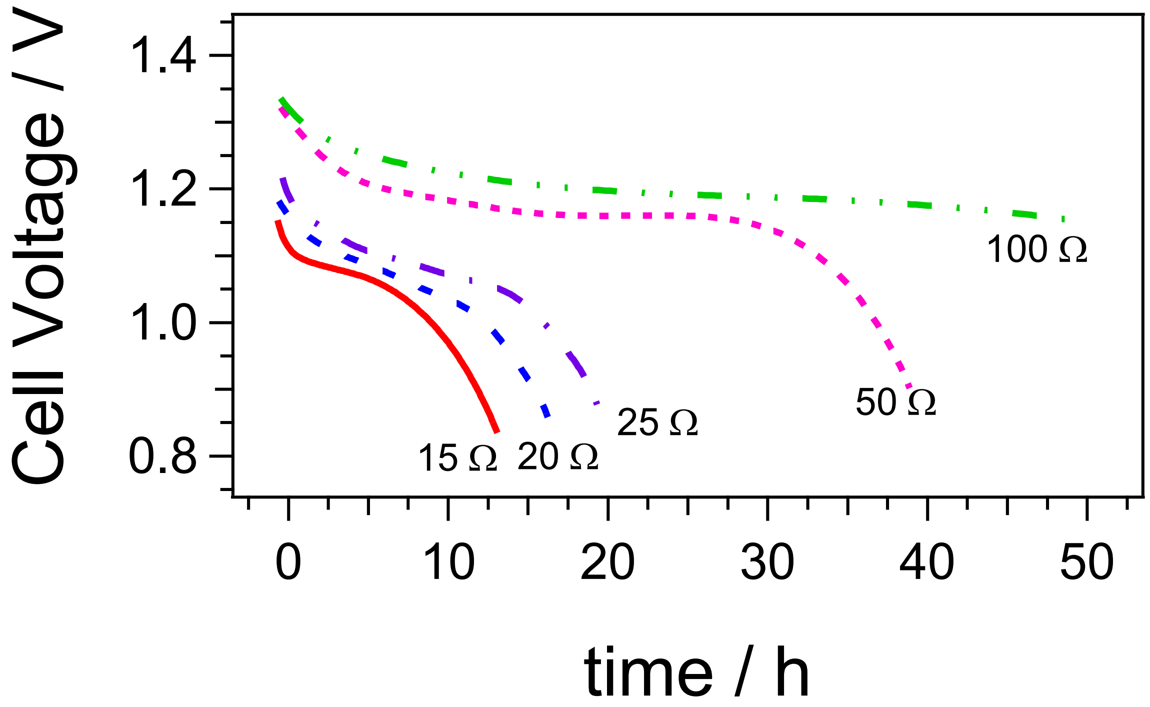
The Zinc – Mercury oxide system



Cross-section of a typical zinc-mercury oxide button cell

Attention is drawn to the sophisticated engineering design of this cell, which has provision doe automatic venting of any pressure caused by H_2 evolution, with any electrolyte displaced being absorbed in the safety sleeve between the inner and outer case.

The Zinc – Mercury oxide system



Discharge characteristics of 1 Ah zinc-mercury oxide button cell under continuous load at room temperature

Mercury cell have practical specific capacities of up to 400 Ah dm^{-3} and specific energy of 550 Wh dm^{-3}. in addition, they have particular flat discharge characteristics even under conditions of continuous discharge.

The flat part of the curve is known as the ‘equilibrium region’ and may be extend to 97% of the cell capacity at low current drains (e.g. 1 mA for a 20 mm diameter button cell).

The Zinc – Mercury oxide system

Momentary short circuits do not damage the cell and voltage recovery is rapid.

Storage behaviour is good, with over 90% of the initial capacity retained after one year.

Low T performance is not particularly favorable, although it is improved if the wound anode configuration is used, especially if the current demands are low or intermittent.

Power sources based on the zinc-mercury oxide system are particularly suited to a wide range of applications, mainly concerned with miniature portable electronic equipment, where a relatively constant voltage is required throughout long discharge periods.

In addition such cells are used as voltage reference standards in regulated power supplies, potentiometers, chart recorders, etc…

The market is shared with more expensive zinc-silver oxide system.

The Zinc – Silver oxide system

The cell may be written as:

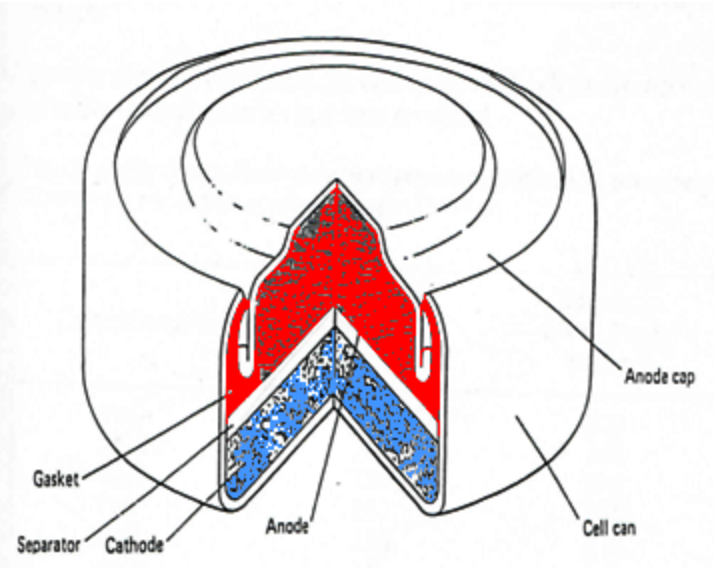
$$Zn_{(s)}\left|ZnO_{(s)}\right|KOH_{(aq)}|Ag_2O_{(s)},C_{(s)}$$

The main features of zinc-silver oxide cells are similar those of the zinc-mercury oxide system, except for a higher OCV and significantly increased cost.

The overall cell reaction is:

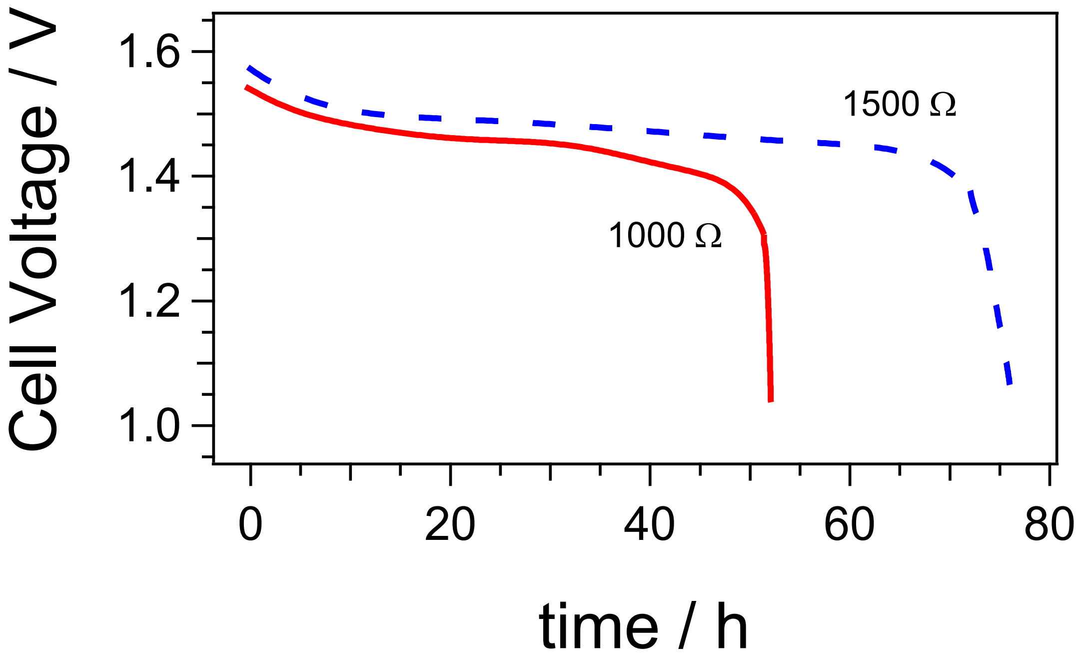
$$Zn_{(s)} + Ag_2O_{(s)} \rightarrow ZnO_{(s)} + Ag_{(s)}$$

The e.m.f. Calculated from Latimer's table of free energies is 1.593 V which agree well with the OCV of commercial cell of 1.60 V.



Cutaway view of a typical zinc-silver oxide button cell (by courtesy of Union Carbide)

The Zinc – Silver oxide system



Discharge characteristics of 75 mAh zinc-silver oxide hearing aid cell under continuous load at room temperature

Electronic watches and other devices with liquid crystal diode (LCD) displays require currents of 3-10 µA and high resistance batteries with NaOH electrolyte are suitable. Watches with light emitting diode (LED) displays or with LCD displays together with additional electrical illumination or alarms, on the other hand, require batteries with low internal resistance which can maintain a stable voltage while supplying current pulses of up to 70 mA for one or two seconds. Cells for such applications use KOH electrolyte. This electrolyte is also used for hearing aid batteries where continuous current drains of 1-2 mA are typical.

The Zinc – Silver oxide system

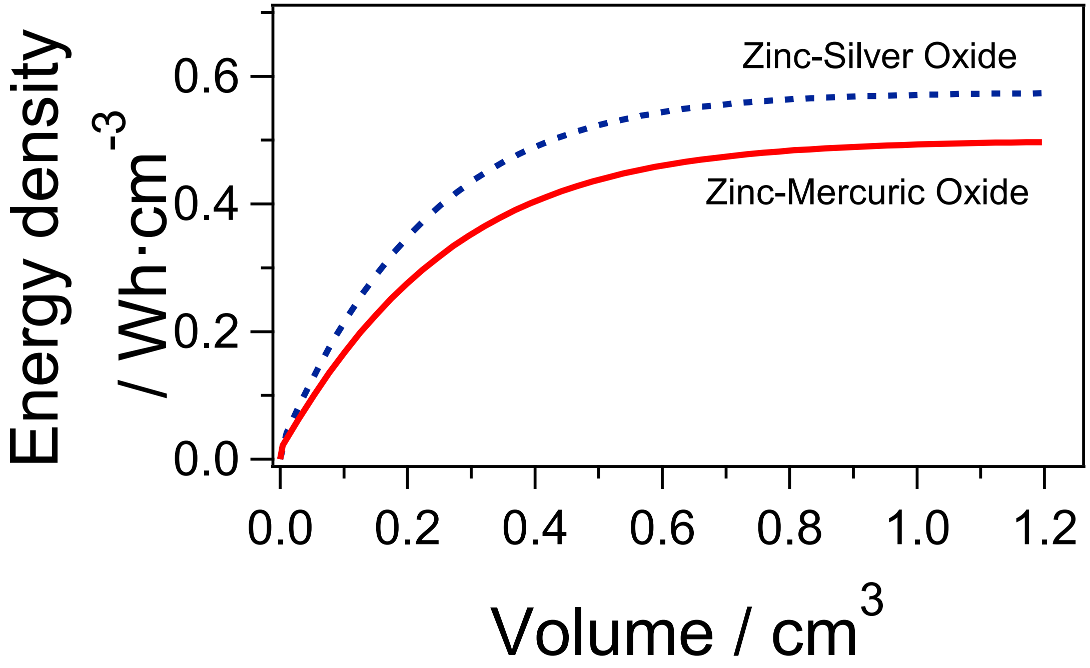
Another application for somewhat large zinc-silver oxide cells is in the production of high-voltage, high capacity reserve batteries for military equipment: e.g. for missile guidance systems and electrically driven torpedo motors.

A number of primary cells using zinc and aqueous KOH electrolyte but with alternative cathode materials have been developed.

Cathode material	Mid-Life Voltage	Volumetric energy density / Wh dm^{-3}
MnO_2	1.30	230
NiOOH	1.55	230
Ag_2O	1.55	450
CuO	0.90	500
HgO	1.35	530
AgO	1.55	600
Air	1.25	950

Practical energy density of miniature alkali button cells (∅ 11.6 mm; h 4.2 mm) with zinc anodes at a discharge rate of 5-10 μA

The Zinc – Silver oxide system



Energy density as a function of total volume for the zinc-mercury oxide and the zinc-silver oxide systems (by kind permission of P. Ruetschi, Leclanché S.A., Yverdon, Switzerland)

The primary objective of miniature battery design is to maximize the energy density in a small container.

A compromise must be reached, however, since volumetric energy density decreases as cell volume decreases and the 'dead volume' due to containers, seals, etc…, becomes increasingly significant.

Metal-air batteries

A number of cells have been developed which make use of the O_2 of the air as the cathodic reactant. The so-called ‘air-depolarized cells’ are an example of a **hybrid cell**

The most obvious advantages of the oxygen cathode is that it has low weight and infinite capacity. Consequently, prototype D-size cell based on the zinc-air system have been shown to have twice the overall practical capacity of zinc-mercuric oxide cells (and 10 time that of a standard Leclanché cell) when subjected to a continuous current drain of 250 mA. In the larger industrial cells energy densities of up 200 Wh kg^{-1} and specific capacities of 150 Ah dm^{-3} may be obtained.

On the other hand, a catalytic surface must be provided for efficient charge transfer at the oxygen cathode, and by its nature, the electrode is susceptible to concentration polarization.

Metal-air batteries

THE OXYGEN ELECTRODE

The oxygen electrode has been the subject of intensive study for many years. The electrode reaction is complex and is greatly affected by the electronic conductor and electrolytic used. In basic solution it may be considered as a two stage process: only the first of these is reversible. The two steps may be written as:

$$O_{2,(aq)} + H_2O_{(l)} \rightleftharpoons HO^-_{2,(aq)} + OH^-_{(aq)}$$

and

$$HO^-_{2,(aq)} + H_2O_{(l)} + 2e^- \rightarrow 3OH^-_{(aq)}$$

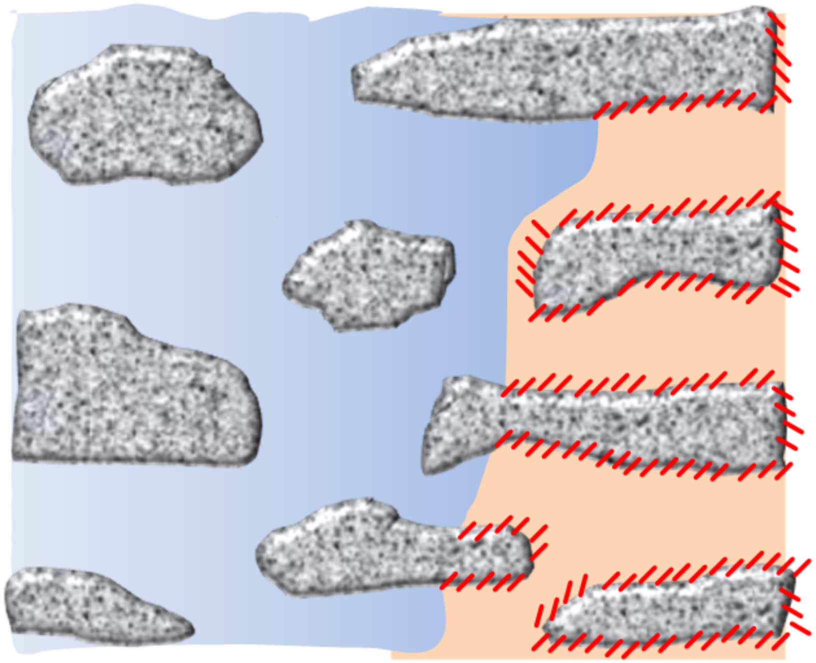
In addition other processes may occur such as the reaction of the hydroperoxide ion with the conductor to form metal-oxygen bonds which in turn may be reduced. The hydroperoxide ion may itself decompose to reform oxygen, etc…. The potential of an oxygen electrode is invariably a mixed potential with a value of about 1.0 V on the standard hydrogen scale at zero current drain.

Metal-air batteries

THE OXYGEN ELECTRODE

Since the electrode reaction can only occur in the region where solid, liquid and gaseous phases come together, the construction of oxygen electrodes, for practical cells is designed to maximize the interfaces between them.

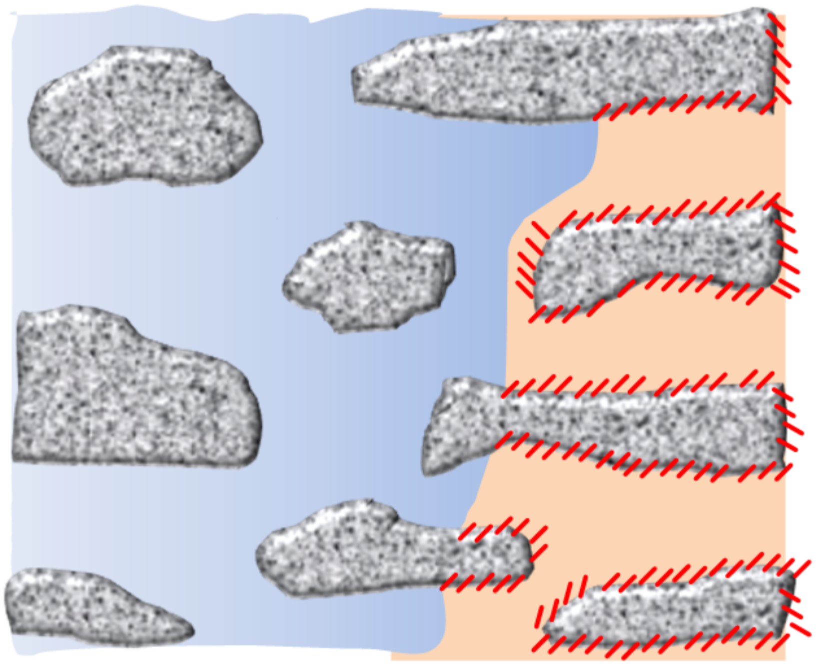
This may be achieved, for instance, by using porous nickel or carbon treated with metal or metal oxide catalysts (Kordesch electrodes).



Schematic view of the interphase at a porous matrix air electrode

Metal-air batteries

THE OXYGEN ELECTRODE



Schematic view of the interphase at a porous matrix air electrode

The pores are made accessible to both electrolyte solution and air and to prevent flooding and eventual leakage of the former.

The surfaces of the electrode which are exposed to air are impregnated with a water-repellent coating using paraffin wax or a synthetic polymer.

It should be noted that oxygen electrodes of this type would be able to pass much larger currents if they were supplied with pure O_2 rather than air.

Metal-air batteries

THE OXYGEN ELECTRODE

The electrolyte for zinc-based cells is always caustic alkali.

Calcium hydroxide is sometimes added to remove zinc ions as insoluble $CaZn_2O_3x\ 5H_2O$.

A caustic alkali electrolyte is effectively buffered against OH^- ion production by the oxygen cathode, so that OH^- concentration polarization is not serious.

An electrolyte can readily become contaminated with carbonate by reaction with CO_2 of the air.

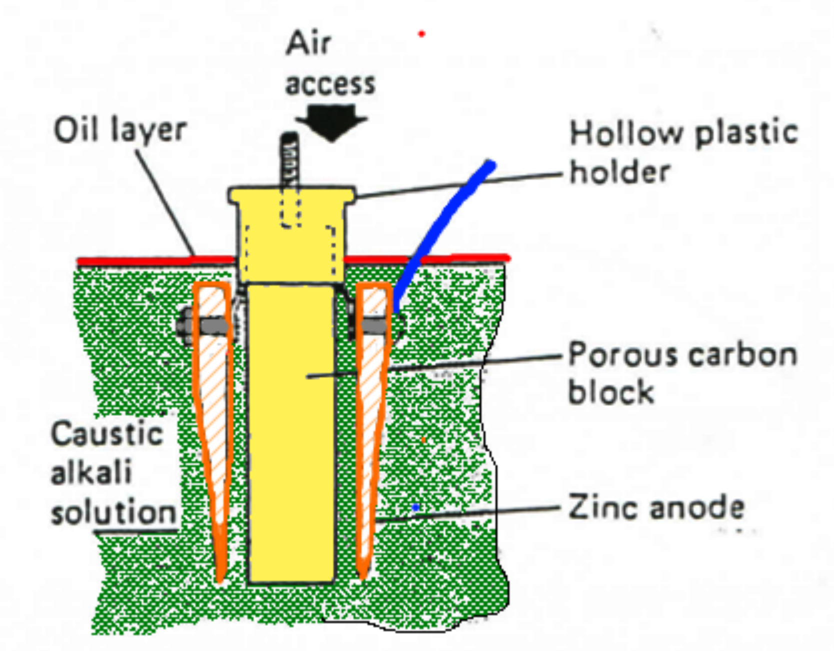
NaOH is substituted by KOH in zinc-air cells intended for low temperature use.

Oxygen electrodes used with the neat neutral electrolytes suitable for aluminum and magnesium anodes are more subject to polarization and are limited to lower current drain applications.

Metal-air batteries

ANODES

Four metals have been studied extensively for use in this type of system, namely Zn, Al, Mg and Li. However the last three metals suffer form severe corrosion problems during storage and Mg-air and Al-air cells are generally operated either as ‘reserve’ systems in which the electrolyte solution is added to the cell only when it is decided to commence the discharge, or as ‘mechanically rechargeable’ batteries which have replacement anode units available.



The lower energy and power density of zinc is compensated for by the ease with which serious corrosion may be inhibited, so that zinc is by far the most commercially important anode in primary metal-air cells.

Cross-section of the electrode assembly of an early 500 Ah mechanically rechargeable zinc-air wet cell, used for railway signalling applications

Metal-air batteries

ANODES

In basic solution, unsaturated with zincate ions, the anode reaction may be written as:

$$Zn_{(s)} + 4OH^{-}_{(aq)} - 2e^{-} \rightarrow ZnO^{2-}_{2,(aq)} + 2H_2O_{(l)}$$

When the solution becomes saturated with zincate, zinc oxide is formed:

$$Zn_{(s)} + 2OH^{-}_{(aq)} - 2e^{-} \rightarrow ZnO_{(s)} + H_2O_{(l)}$$

A number of techniques have been used to prevent degradation of battery performance caused by ZnO passivation.

In the early wet cells, despite the penalty of reduced energy density, sufficient electrolyte was added to allow most of the zinc to dissolve.

In more modern construction, anodes are made by compacting powdered zinc onto brass current collectors or by electrolytic reduction of pasted sheets, to form a porous mass with a high area/volume ratio. In this configuration the oxide does not significantly block further oxidation of zinc.

Metal-air batteries

ANODES

In addition, most of the electrolyte required may be incorporated within pores.

A carefully positioned current collecting grid is a necessity for such a cell since, by its nature, it is always anode limited.

TYPICAL CELLS

Zinc-based industrial primary cells range in size from 90 Ah cylindrical cells used mainly in telecommunications, hazard warning lights, etc…, to 2000 Ah cells designed for inshore navigation beacons, standby power and railway track and signaling circuits.

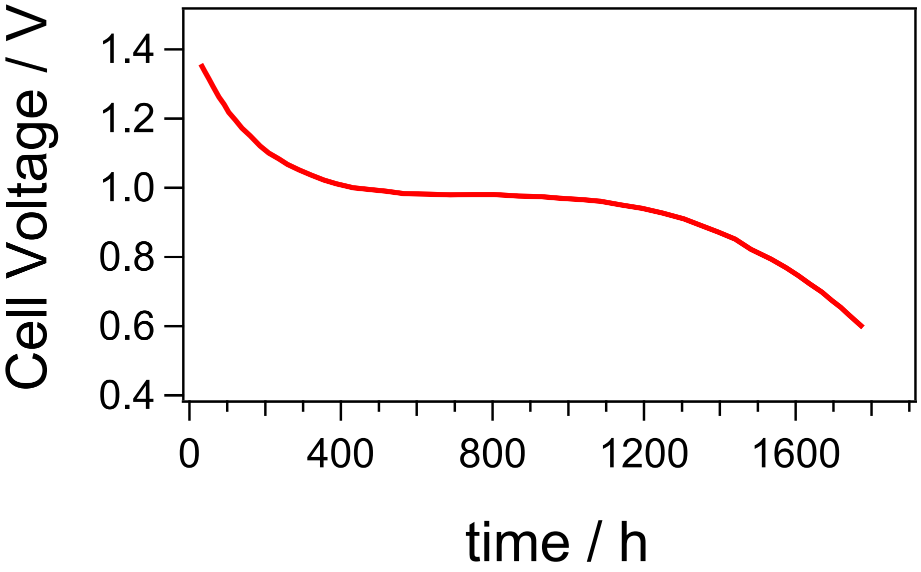
The cell may be written as:

$$Zn_{(s)}\left|NaOH_{(aq)}\right|C_{(s)}, O_{2,(g)}$$

and the nominal OCV is 1.4 V.

Metal-air batteries

TYPICAL CELLS



Continuous discharge curve through 2 Ω load of a 750 Ah zinc-air cell. Such cells have a 5° intermittent pulse capacity and good capacity retention. (by courtersy of SAFT (UK) Ltd.)

With the largest cells continuous discharge drains of 1A and intermittent discharges of 2.5 A are possible. The internal resistance of such cells is low (≈ 0.1 Ω).

Cells are also formed into batteries with nominal OCV of 7.2 V for electric fence activators.

Alternatively, banks of eleven individual cells are used to operate 10 V railway signal motors: such applications require a current drain of 3 A for 5-10 seconds, perhaps one hundred times per day.

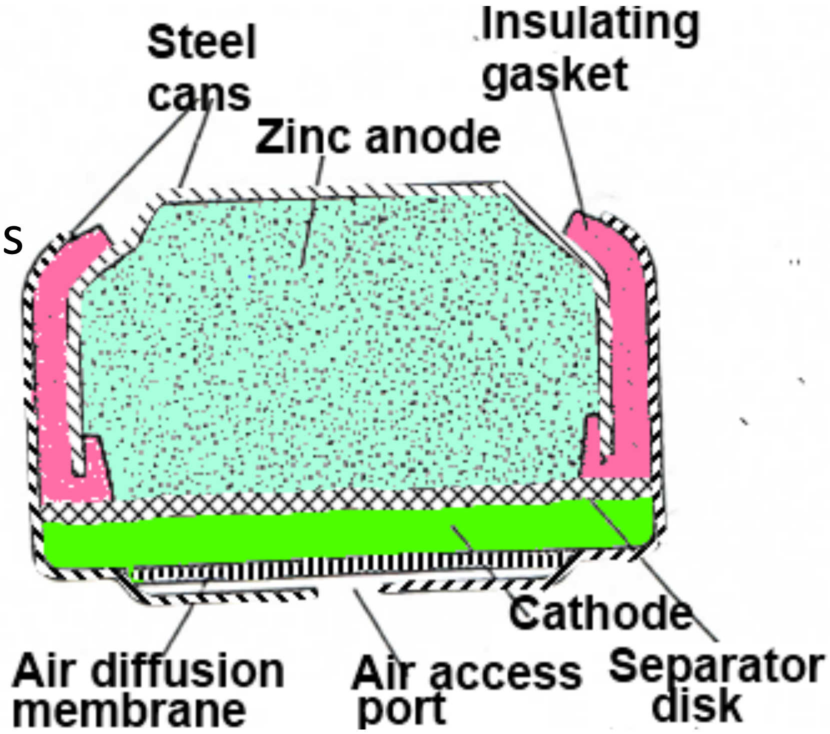
Practical energy densities of up to 310 Wh·kg^{-1} may be obtained.

Metal-air batteries

TYPICAL CELLS

A miniature ‘air-depolarized’ zinc cell is shown, such cells are used for hearing aids and similar devices: they have a similar configuration to the more conventional mercury or silver button cell, but a much higher capacity for the same volume, e.g. 560 Ah·dm^{-3} (190 Ah · kg^{-1}).
Zinc-air cells with electrolytes based on NH_4Cl and a similar OCV are also manufactured:

$$Zn_{(s)}\left|NH_4Cl_{(aq)}\right|C_{(s)}, O_{2,(g)}$$



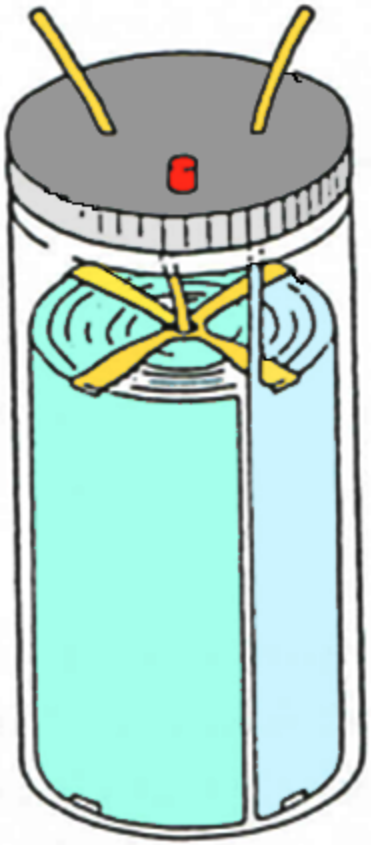
Cross-section of Zinc-air button cell (by courtesy of Gould)

The cell reaction can be written as

$$2Zn_{(s)} + 4NH_{(aq)}^{+} + 4Cl_{(aq)}^{-} + O_{2,(g)} \rightarrow 2Zn(NH_3)_2Cl_2 + 2H_2O_{(l)}$$

Secondary aqueous electrolyte cells

THE LEAD-ACID CELL



Original Planté spiral wound lead-acid cell

These range in size from 5 Wh cells to 100 Wh starting, lighting and ignition (SLI) systems, and to projected 10 MWh load leveling modules.

The great success of this system is due to a number of favorable factors such as:

- the relatively low cost and availability of raw materials (lead and sulphur),
- ease of manufacture,
- long cycle life,
- favorable electrochemical characteristics.

The performance of the lead-acid cell has been improved through more than a century of continuous research and development.

The lead-acid cell

The lead-acid cell can be represented schematically as having a negative electrode of porous lead (lead sponge) and a positive electrode of lead dioxide, PbO_2, both immersed in aqueous solution of sulphuric acid:

$$Pb_{(s)}\left|PbSO_{4,(s)}\right|H_2SO_{4,(aq)}\left|PbSO_{4,(s)}\right|PbO_{2,(s)}|Pb_{(s)}$$

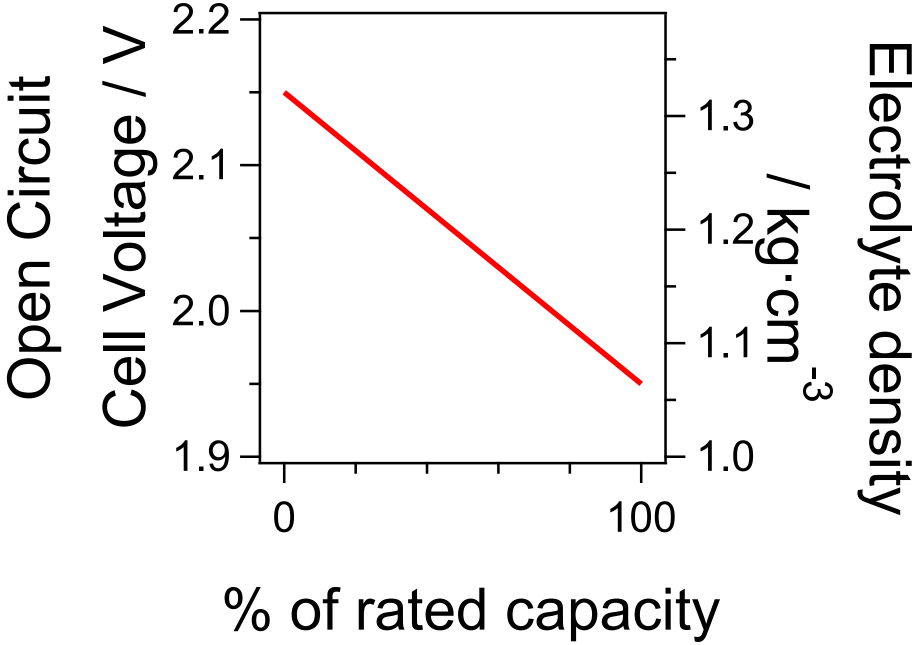
The overall electrochemical processes can be represented by:

$$Pb_{(s)} + PbO_{2,(s)} + 2H_2SO_{4,(aq)} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} 2PbSO_{4,(s)} + 2H_2O_{(l)}$$

As the cell is discharged, sulfuric acid is consumed and water is formed. Consequently the electrolyte composition and density vary from about 40% by weight of H_2SO_4 (1.30 kg·dm^{-3}) at full charge, with associated OCV of 2.15 V at 25°C, to about 16% by weight of H_2SO_4 (1.10 kg·dm^{-3}) when fully discharged, with an OCV of 1.98 V.

The change in electrolyte specific gravity provides a convenient method of determining the state of charge of a cell.

The lead-acid cell



Approximate OCV and electrolyte density as a function of percentage service capacity for the lead-acid cell

The OCV depends on the sulphuric acid (and water) activity and T and may be predicted with accuracy from thermodynamic free energy values.

The discharge process also results in the formation of insoluble lead sulphate on both electrodes. This material is a very poor electrical conductor and its deposition in a dense, fine-grained form can shield and passivate both electrodes, so that the practical capacity of a cell can become severely restricted – to as little as 5-10% of the theoretical capacity for large current densities. As discharge proceeds, the R_i of the cell rises, due to $PbSO_4$ formation and the decrease in electrolyte conductivity as H_2SO_4 is consumed.

The lead-acid cell

POSITIVE ELECTRODES

The electrochemical reactions at the positive electrode are usually expressed as:

$$PbO_{2,(s)} + 4H^{+}_{(aq)} + SO^{2-}_{4,(aq)} + 2e^{-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_{4,(s)} + 2H_2O_{(l)}$$

In practice the bisulphate ion, HSO_4^-, is rather weak acid (pKa = 1.99 at 25°C), so that for the sulphuric acid concentrations used in practical cells the reactions

$$PbO_{2,(s)} + 3H^{+}_{(aq)} + HSO^{-}_{4,(aq)} + 2e^{-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_{4,(s)} + 2H_2O_{(l)}$$

May be considered a more accurate description of the electrode process.

The lead-acid cell

POSITIVE ELECTRODES

Both PbO_2 and $PbSO_4$ are slightly soluble, and it is probable that soluble leaf species are involved in the reaction mechanism. In the absence of mass transport limitations, it is considered that the process:

$$PbO_2(H^+)_{2,(surface\ )} + e^- \longrightarrow Pb(OH)^+_{2,(surface\ )}$$

is rate determining for the discharge reaction. The PbO_2 is found to vary slightly in stoichiometry at different stages in the cycle. Immediately after charge it may have a composition as high as $PbO_{2.05}$.

In order to obtain optimum current densities, it is necessary to use a highly porous structure so that the solid/electrolyte contact area is large.

The fully charged positive electrode is therefore composed of a mass of small PbO_2 crystals connected to each other to form a continuous porous network.

The lead-acid cell

POSITIVE ELECTRODES

The electrode porosity is important for another reason, since it makes allowance typical SLI battery the real area of the positive electrode is calculated to be 50-150 m^2 per Ah of capacity ($6\text{-}20 \cdot 10^{-3}$ $Ah \cdot m^{-2}$).

As current is drawn from the cell, the positive electrode voltage is depressed due to concentration polarization as sulphuric acid within the pores is consumed. This effect is more marked for partially discharged cells since the pore volume decreases as lead sulphate is formed.

An important feature of the positive electrode discharge concerns the nature of the $PbSO_4$ deposit since the formation of dense, coherent layers can lead to rapid electrode passivation.

The lead-acid cell

POSITIVE ELECTRODES

Lead dioxide exists in two crystalline forms, rhombic (α-) and tetragonal (β-), both of which are present in freshly formed electrode structures. Since $PbSO_4$ and α-PbO_2 are isomorphic, crystal of PbO_2 of this modification tend to become rapidly covered and isolated by $PbSO_4$ and their utilization is less than that of the tetragonal β-form.

As the latter, is the thermodynamically more stable of the two, some transformation of α- into β-PbO_2 may occur during the life of a battery, with consequent improvement in its performance.

Positive electrodes are manufactured in three forms, as:

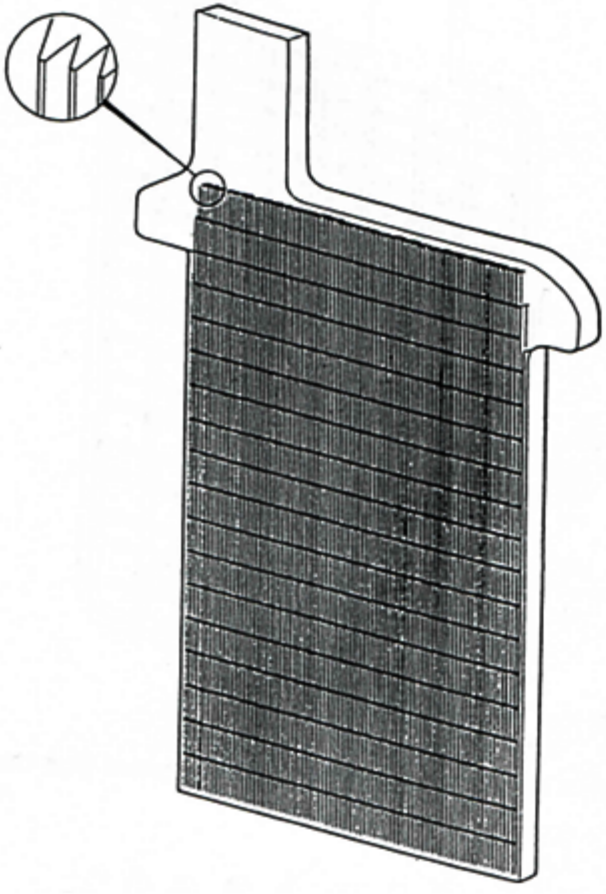
i) Planté plates,

ii) Pasted plates,

iii) Tubular plates.

The lead-acid cell

POSITIVE ELECTRODES



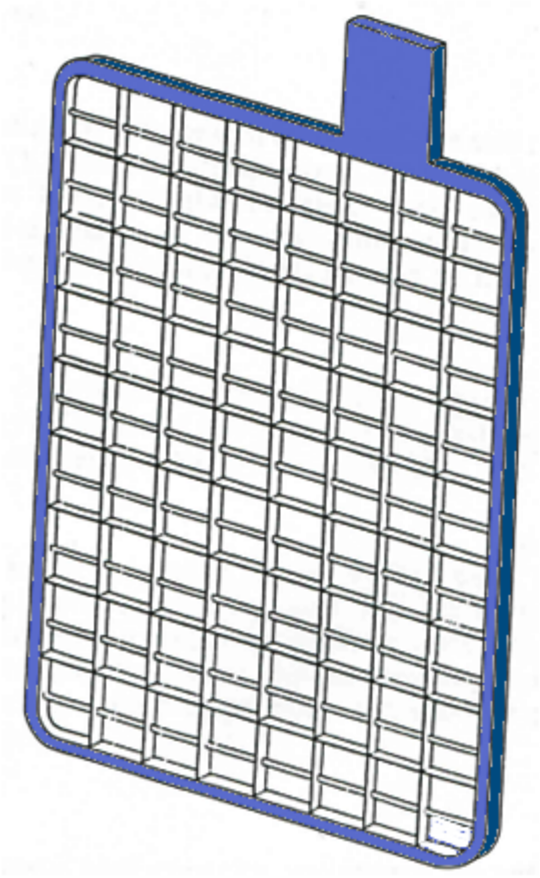
Planté plate. Details shows the grooves which increase the effective area of the plate.

In Planté plates, the positive active materials is formed by electrochemical oxidation of the surface of a cast sheet of pure lead to from a thin layer of PbO_2.

The plate generally has a grooved surface to increase its surface above its geometric area by a factor of 3-10. Such plates have a very long life since they have a large excess of heavy (and expensive) and their mechanical strength is poor, so that their use is confined to stationary battery applications in which long service life is important.

The lead-acid cell

POSITIVE ELECTRODES



Typical lead-acid battery grid: this acts as a framework to hold the active material in place.

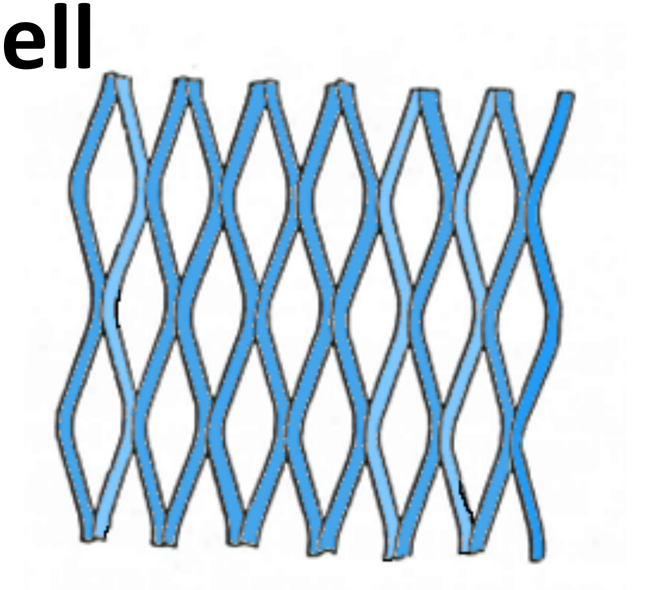
In 1880, Fauré proposed coating the lead sheet with a ‘paste’ of PbO_2 and sulphuric acid in order to increase the capacity of the system. It was soon found that the paste would be more readily applied to an open grid support, rather than to a lead sheet.

Grids are designed to ensure a low internal resistance for the cell and to minimize shedding of active material on cycling. Shedding causes loss of capacity, and dislodged material can accumulated on the battery case floor where it can give rise to short circuits between positive and negative plates.

The lead-acid cell

POSITIVE ELECTRODES

Additions of small quantities of Sn are made to the lead to improve its coating properties, while Sb, Ca or Se are added to form alloys with better stress resistance.



Expanded metal grid

Pb-Sb was the firs ally used and still remains the most popular.

Sb (1.5-8%) greatly improves the mechanical properties of grids and connector bars, but also increases their electrical resistance, accelerates the self discharge of the cell, and reduces cycle efficiency. Further, during recharge, poisonous SbH3 gas can be formed.

Research is continuing into the development of better alloys. Pb-Ca grids are superior in many ways. The use of Se has allowed the manufacture of low-antimony grid of adequate mechanical strength.

The lead-acid cell

POSITIVE ELECTRODES

The main component of the paste used to fill the grid is known as lead dust, and consists of a carefully milled mixture of metallic lead and lead oxide.

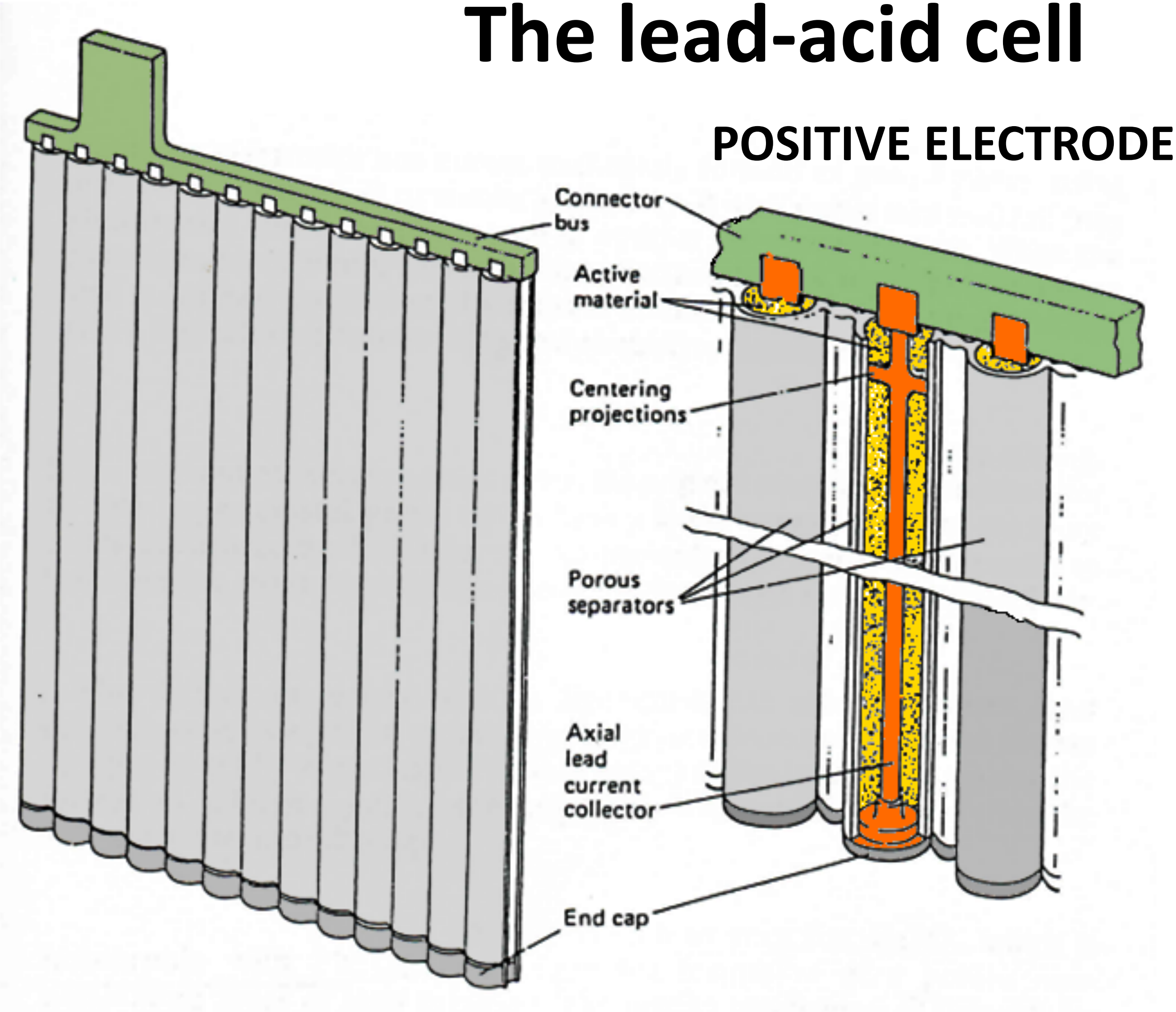
Water and sulfuric acid are added in a predetermined sequence, together with minor components and strengthening fibers, and the resulting slurry is loaded onto the grids and ‘cured’ or dried to produce a crack-free plate, with good adherence to the grid.

Pasted plates have a relatively high capacity and power density, but are not mechanically strong.

They are used extensively in SLI and similar batteries.

The lead-acid cell

POSITIVE ELECTRODES: TUBULAR PLATES



a) Tubular plates for lead-acid cells

b) Cross-section showing central lead current collector, active material and porous separators

The lead-acid cell

POSITIVE ELECTRODES: TUBULAR PLATES

Tubular plates (also known as ‘armoured’ or ‘clad’ plates) consist of a row of tubes containing axial lead rods surrounded by active material.

The tubes are formed of fabrics such as terylene or glass fiber or of perforated synthetic insulator which are permeable to the electrolyte.

They generally have a circular cross-section, but square, rectangular and oval tubes are also manufactured. Tubular plates are sufficiently strong to withstand continuous vibration and are resistant to shedding.

They are also able to sustain many deep discharges without loss of integrity and are therefore suitable for applications such as EV traction.

The lead-acid cell

NEGATIVE ELECTRODES

The reactions of the negative electrode are generally given as:

$$Pb_{(s)} + SO_{4,(aq)}^{2-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_{4,(s)} + 2e^{-}$$

but as discussed previously are more correctly expressed as:

$$Pb_{(s)} + HSO_{4,(aq)}^{-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_{4,(s)} + H_{(aq)}^{+} + 2e^{-}$$

Negative electrodes are almost exclusively formed of pasted plates, using either fine mesh grids or coarse grids covered with perforated lead foil (**box plates**), and the same paste used in positive plate manufacture. When the paste is reduced under carefully controlled conditions, highly porous **sponge lead** is formed consisting of a mass of acicular (needle-like) crystals which give a high electrode area and good electrolyte circulation.

The lead-acid cell

NEGATIVE ELECTRODES

On deep cycling, however, and especially at high rates, the original morphology tends to alter to give larger crystal grains which have a lower overall area and are more easily passivated by PbSO4 layers. Additions (≈ 1%) are therefore made to the negative mass to minimize crystallization of the spongy $PbSO_4$.

Surface-active materials such as ligno-sulphonic acid derivatives (and substances deriving from soot or lampblack) are known as **expanders** and are thought to act by lowering the surface energy of the lead and so making the formation of large crystals less energetically favorable. They also affect the $PbSO_4$ morphology.

Additives such as very fine $BaSO_4$, which is isomorphic with $PbSO_4$, encourages the formation of a porous non-passivating layer of $PbSO_4$. The precise mechanism of the additive effects is complex and not completely understood. It is known that BaSO4 and the organic additives interact since together they are much more effective than the sum of their individual contributions.

The lead-acid cell

ELECTRO FORMING

Forming is defined as the procedure undertaken, usually before final assembly in the battery case, to convert the active material in the positive and negative plates into their fully charged condition.

In effect, the forming process is equivalent to the first charge, but the electrolysis operation is carried out:

- ✓ using carefully controlled conditions of temperature and electrolyte composition,
- ✓ at low current density (typically $< 100\ \mathrm{A \cdot m^{-2}}$),

in order to achieve complete conversion throughout the electrode masses while retaining adherence and porosity.

SLI batteries are nowadays often supplied in a dry charged state and are activated simply by filling with electrolyte.

Plates for such batteries have extra additivies, such as antioxidant in the negative active mass, and forming is followed by one of a number controlled drying processes.

The lead-acid cell

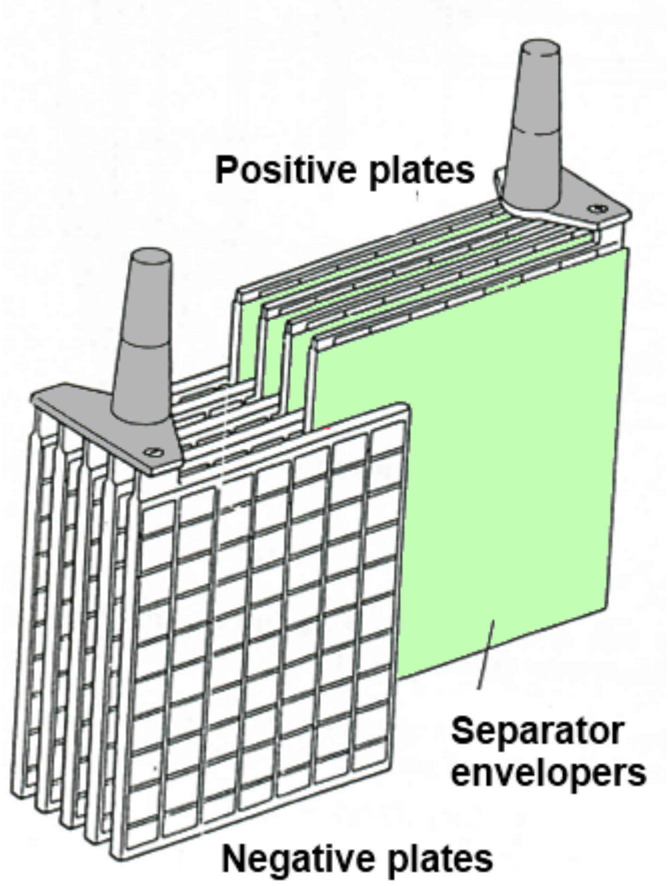
SEPARATORS

Separators are porous insulating sheets which are placed between electrodes of opposite polarity to prevent contact and short circuit between them. They also act ad a barrier to the transport of active material between the plates, mechanically support the positive active mass (so reducing shedding) and prevent dendrite formation.

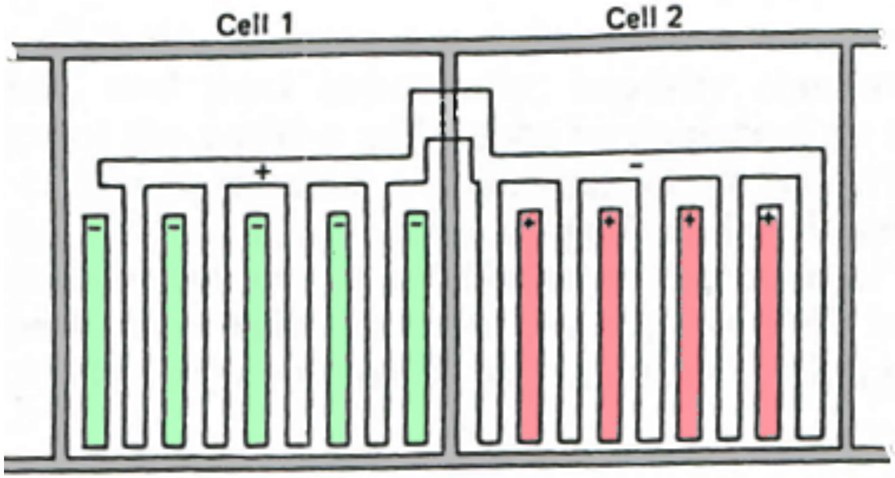
The most popular materials include sintered polyvinylchloride, and extruded polyethylene. Special papers, impregnated with phenolic resins are also in current use. Research is continuing to develop separators which are able to retain very large quantities of electrolyte for use in sealed batteries which can be operated in any orientation. Very efficient thin separators are required for high energy density batteries. Hard rubber or glass fibre is used to fabricate **retainers** which are perforated sheets in contact with the positive plate which protect the separators from its strong oxidizing environment.

The lead-acid cell

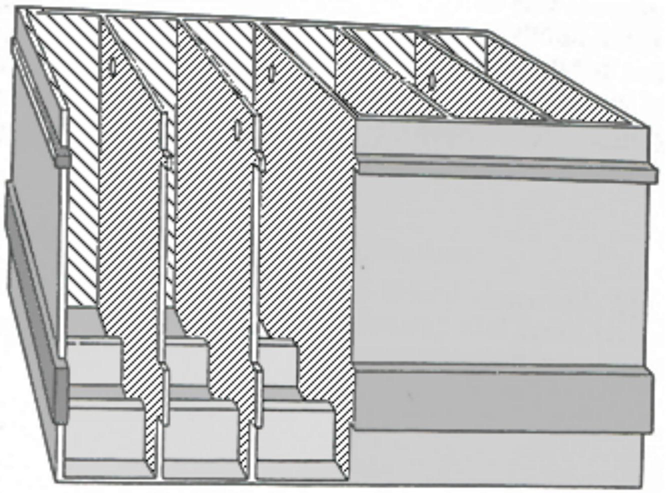
FINAL ASSEMBLY



Interleaving of positive and negative electrode groups (elements) to form a lead-acid cell.



Schematic diagram of lead-acid battery showing through-partition connection



Monobloc injection moulded case

The lead-acid cell

PERFORMANCES

The practical capacity of all such batteries is also dependent on the temperature of operation and is found to drop very rapidly at T < 0°C.

As the system is thermodynamically unstable with respect to H_2 and O_2 evolution, lead-acid cells are subject to self-discharge:

$$PbO_{2,(s)} + H^+_{(aq)} + HSO^-_{4,(aq)} \rightarrow PbSO_{4,(s)} + H_2O_{(l)} + \frac{1}{2}O_{2,(g)}$$

and

$$Pb_{(s)} + H^+_{(aq)} + HSO^-_{4,(aq)} \rightarrow PbSO_{4,(s)} + H_{2,(g)}$$

The rates of these processes are dependent on:

- Temperature,
- Electrolyte composition
- Impurity content (most important)

The lead-acid cell

PERFORMANCES

If Sb is leached out of the positive grid it may be deposited on the negative plate where it catalyzed reaction, because of its relatively low hydrogen overvoltage. The use of low antimony grids and antimony trapping separators reduces the amount of self-discharge. Reaction of the positive plate material with other solution impurities such as Fe^{2+} ions which can be re-reduced at the negative leads to very rapid self-discharge.

Corrosion of the positive grid can occur on charging and over-charging if the metal becomes exposed to the electrolyte. This leads to a progressive weakening of the plate structure and to an increase in the internal resistance of the cell.

The lead-acid cell

PERFORMANCES

If a lead-acid battery is left for a prolonged period in an uncharged state or is operated at too high temperature or with too high an acid concentration, the PbSO4 deposit is gradually transformed by recrystallization into a dense, coarse-grained form.

This process is known as **sulphatation** and leads to severe passivation, particularly of negative plates and therefore inhibits charge acceptance.

It is sometimes possible to restore a sulphatated battery by slow charging in very dilute sulphuric acid.

The lead-acid cell

TYPES OF LEAD-ACID BATTERY AND THEIR APPLICATIONS

Three many types of battery will be briefly described:

- SLI batteries.
- Industrial batteries (traction and stationary)
- Small sealed portable batteries

The order follows their present relative commercial importance.

SLI Batteries

SLI batteries generally have:

- nominal voltage of 12 V and 30-130 Ah capacities for cars,
- 24 V and up to 600 Ah for lorries, construction and military vehicles.

Typical batteries have energy densities of 30 $\mathrm{Wh \cdot kg^{-1}}$ (60 $\mathrm{Wh \cdot dm^{-3}}$) but units with up to 40 $\mathrm{Wh \cdot kg^{-1}}$ (75 $\mathrm{Wh \cdot dm^{-3}}$) may be obtained. Depending on the use, service lifetimes of 3-5 years are normal.

The lead-acid cell

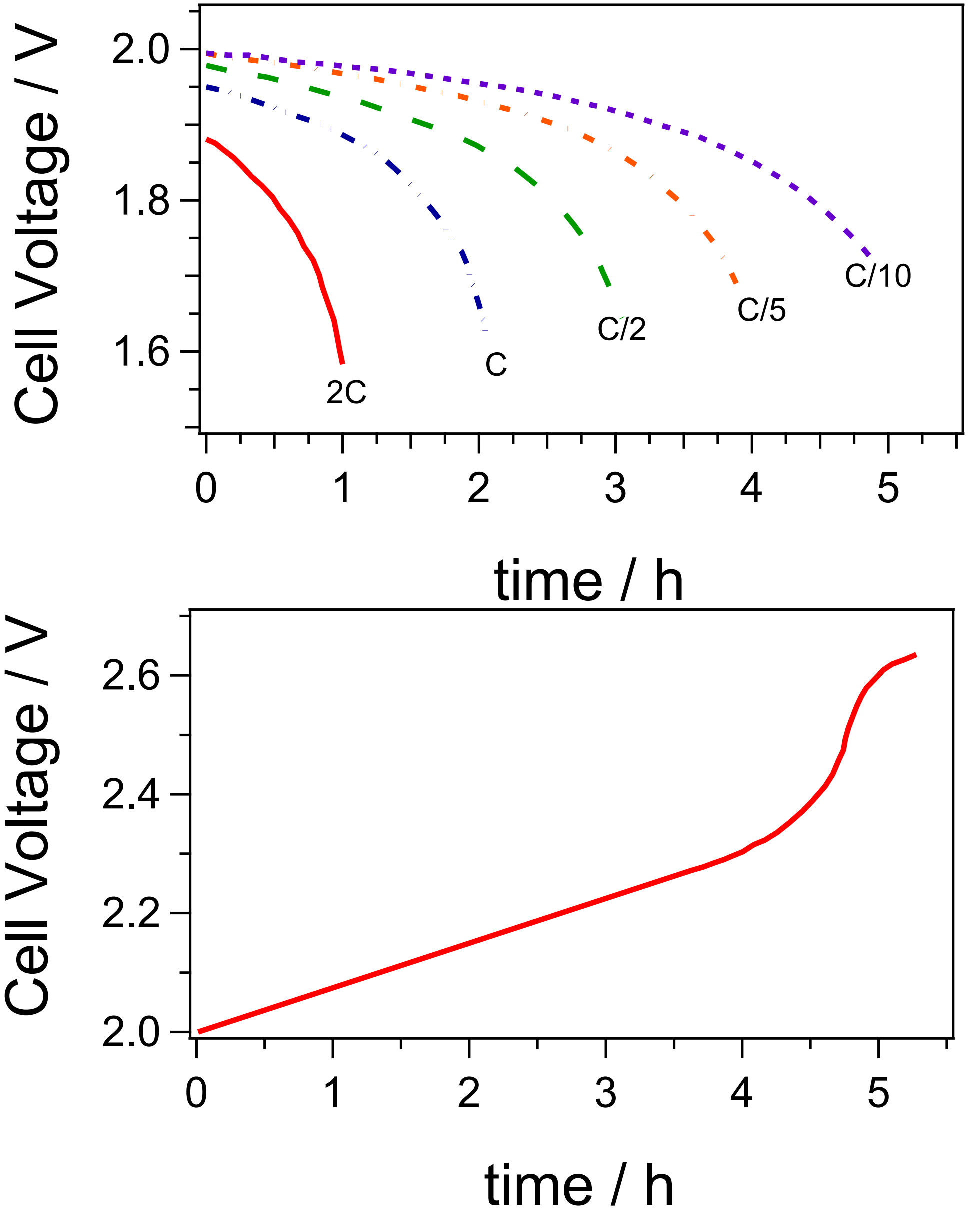
SLI Batteries

For vehicles used in rugged terrain, batteries with tubular positive plates are required.

Over the past ten years, the introduction of batteries described as ‘maintenance free’ (MF) has had an important impact on the SLI market. What this term implies in practice is that no addition of water to the electrolyte is required over a normal service life of 2-5 years.

MF batteries often have their electrolyte immobilized by means of gel formation using silica, calcium sulfate, etc…, or by incorporating it in microporous separators.

The lead-acid cell



Industrial batteries

Motive power batteries are generally of higher quality than SLI batteries. Their most important characteristics are constant output voltage, high volumetric capacity at relative low unit cost, good resistance to vibration and a long service life.

a) ***Discharge curves for a typical lead-acid cell at various rate***
b) ***Charging curve for the lead-acid cell at C/10.***

The lead-acid cell

Industrial batteries

The size and performance of traction batteries vary over a wide range:

- the voltage used may be 12-240 V,
- the capacity of each cell extends from 100 Ah to 1550 Ah or more.

The specific energy of these units is normally in the range 20-30 $\text{Wh}\cdot\text{kg}^{-1}$ (55-77 $\text{Wh}\cdot\text{dm}^{-3}$) and the cycle life is 1000-1500 cycles.

The multi-tubular positive plates give the cell high specific energy and capacity and assure a long cycle life. Positive plates are incorporate glass wool felt and special separators to absorb shocks and vibration, and to prevent shedding of active material.

Traction batteries are used in industrial trucks, e.g. ‘fork-lift’ trucks (in the UK over 60% of all such vehicles are battery powered), milk floats and other delivery vehicles, mining and other tractors, industrial sweepers and scrubbers, golf carts, etc…

The lead-acid cell

Industrial batteries

Stationary batteries fall into two groups:

- ✓ Systems for intermittent use or standby power
- ✓ Load leveling systems

The most important characteristics of the firs group are reliability, long life and low self discharge rate. Such batteries often employ Planté plates; otherwise they use tubular plates or thick pasted plates formed on low antimony grids.

Stationary batteries of this type are used for:

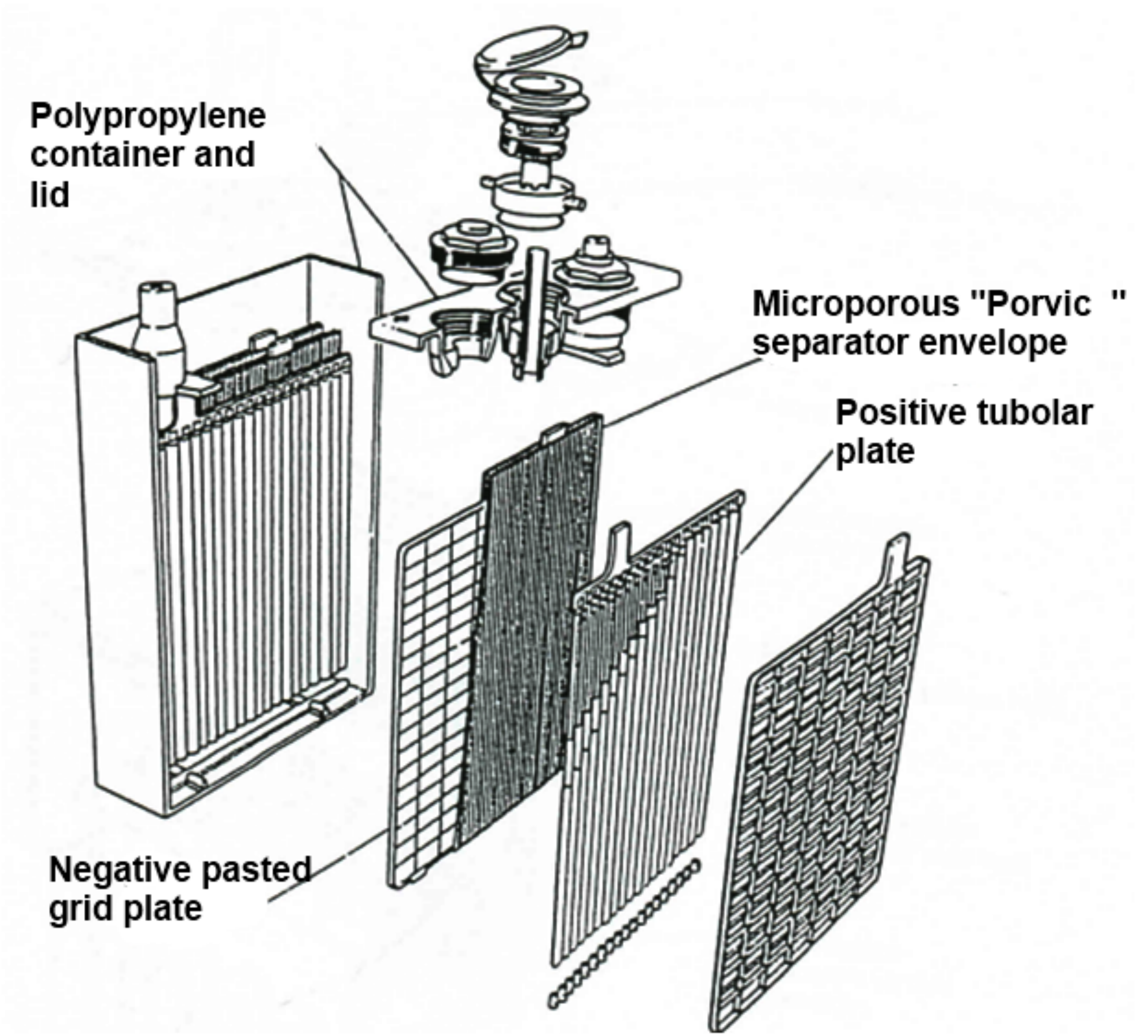
- ✓ telecommunications systems,
- ✓ railroad signaling,
- ✓ track control,
- ✓ standby power.

whether it is necessary to have continuity of service during power cuts and momentary interruptions.

The lead-acid cell

Industrial batteries

Motive power lead-acid cell with tubular positive plates in which the active materials is contained in pre-formed terylene tubes, and negative pasted grid plates surrounded by micro-porous polyvinyl chloride separator envelopes. The case and lid are formed of heat sealed polypropylene (by courtesy of Chloride Industrial Batteries)

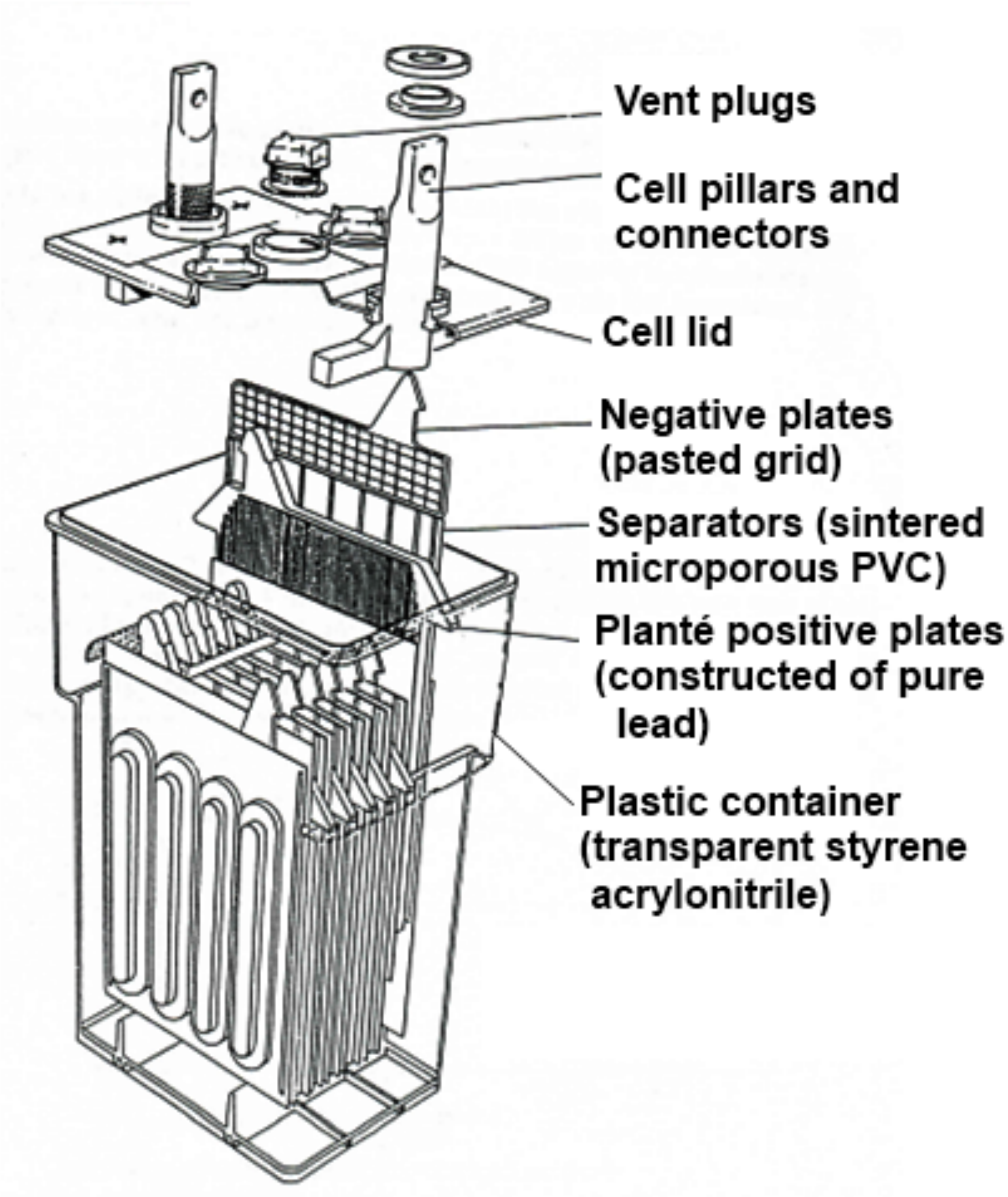


The lead-acid cell

Industrial batteries

The capacity of each cell is in the range 20-2200 Ah at C/10

Standby power high performance Planté cell. The container is fabricated from transparent styrene acrylonitrile which enables the electrolyte level and cell condition to be easily monitored (by courtesy of Chloride Industrial Batteries)



The lead-acid cell

Sealed, portable batteries

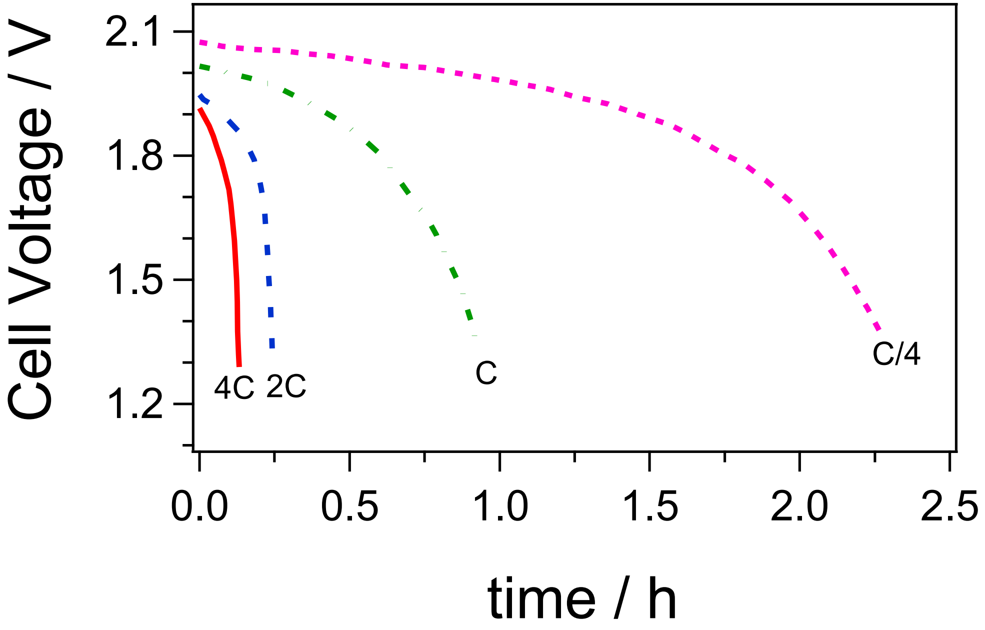
In recent years the market for small, portable lead-acid batteries has grown considerably. These are sealed batteries obtained by assembling cylindrical or rectangular (prismatic) unit cells. They are generally not hermetically sealed since a safety vent is provided to allow gas escape in the event of excessive overcharge.

Positive and negative plates are usually made using a ‘honeycomb’ grid support filled with active materials.

The separators are thin films of porous highly insulating materials which also retain the electrolyte. Usually they contain a non-woven glass microfiber mat which is heat and oxidation resistant. Plates and separators are sandwiched together in cylindrical rolls: this assembly results in a vibration resistant cell with low impedance, low polarization, long life and high utilization.

The lead-acid cell

Sealed, portable batteries



Discharge curve for sealed cylindrical lead-acid cell

These batteries are generally constructed with a range of capacities from 2 to 30 Ah; they give 300 to 2000 cycles according to the particular application.

Further advantages offered by this new type of cell includes:

- ✓ absence of maintenance,
- ✓ good constancy of discharge voltage at up to C/4,
- ✓ ability to sustain short current discharge pulses,
- ✓ low self discharge (typically 6-8% per month) at ambient temperature

in comparison with nickel-cadmium cells.

The lead-acid cell

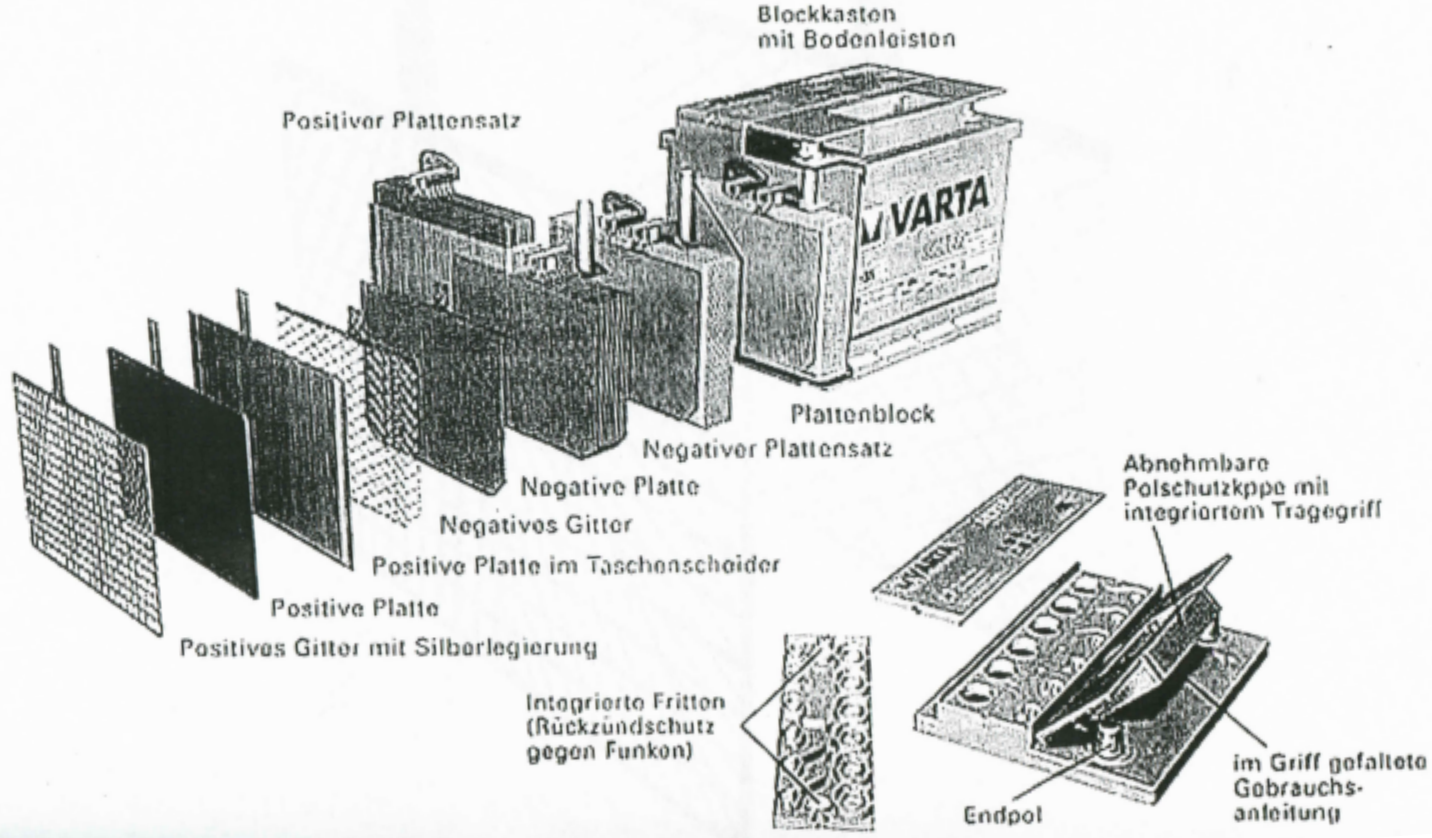
Sealed, portable batteries

Semi-sealed portable lead-acid cells can operate in any orientation without acid leakage and find use in many different applications, such as in electronic cash registers, alarm systems, emergency lighting unit equipment, telephone boxes, switching stations, mini-computers and terminals, electronically controlled petrol pumps, cordless television sets and portable instruments and tools.

The lead-acid cell

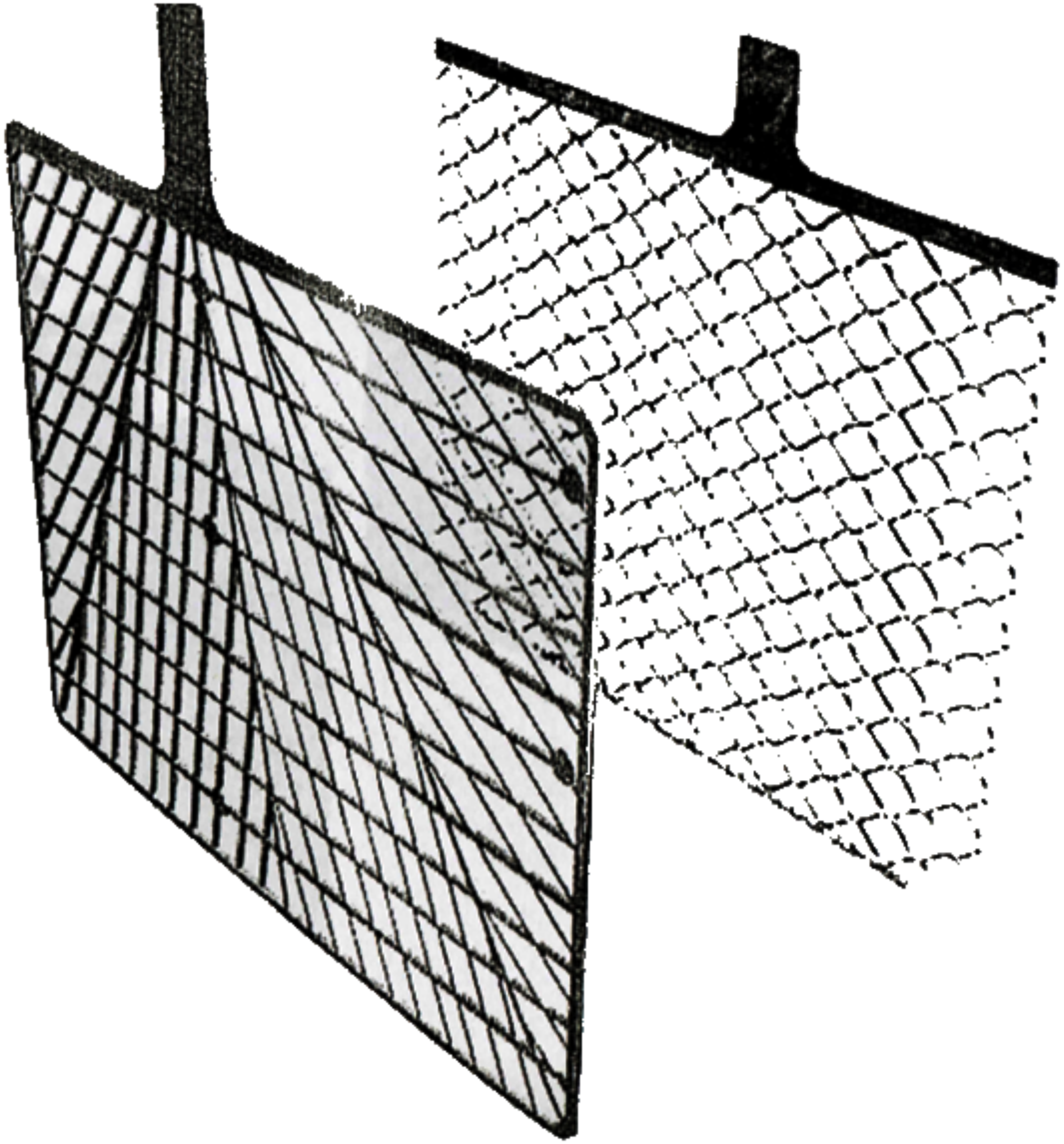
Sealed, portable batteries

Aufbau einer Varta Silver dynamic-Batterie



The lead-acid cell

Sealed, portable batteries

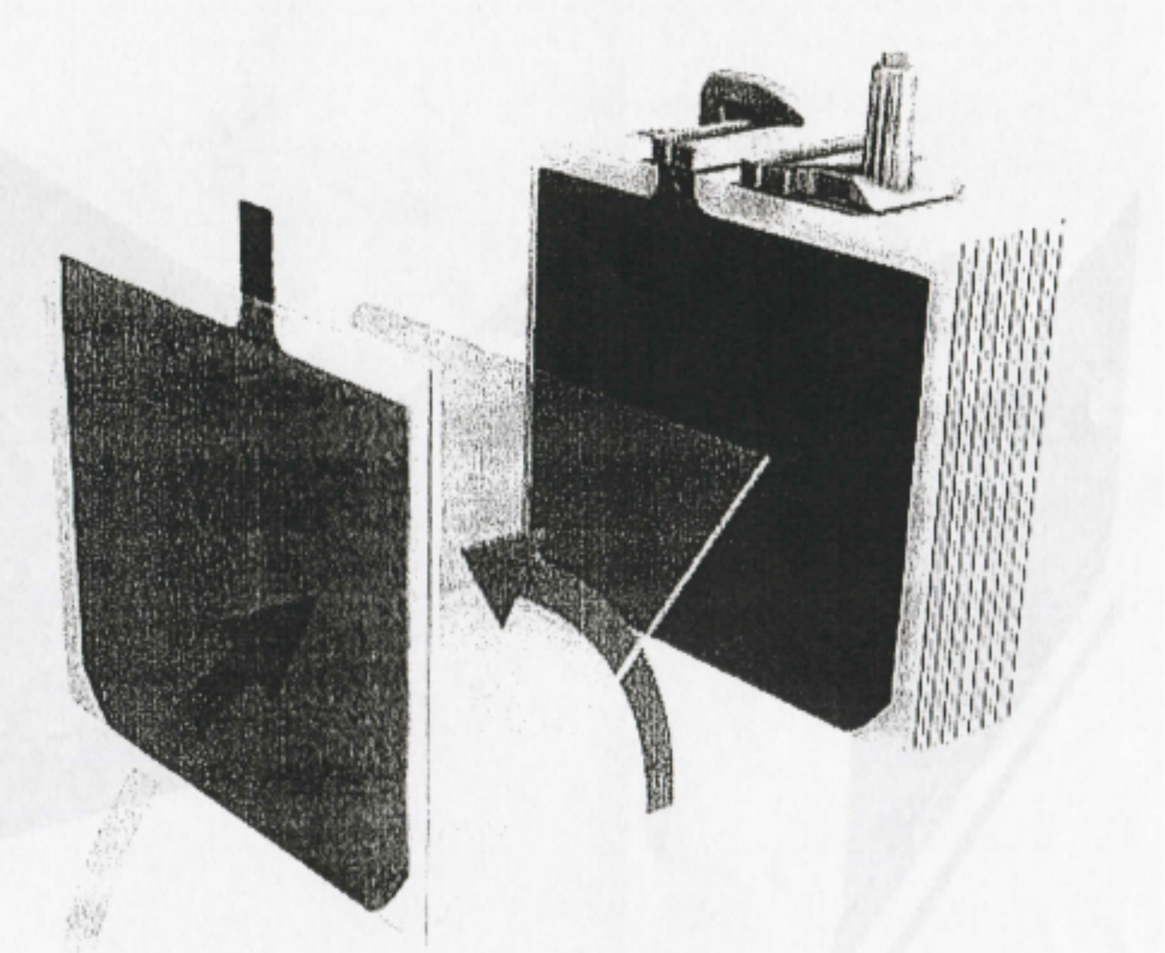


The lead-acid cell

Sealed, portable batteries

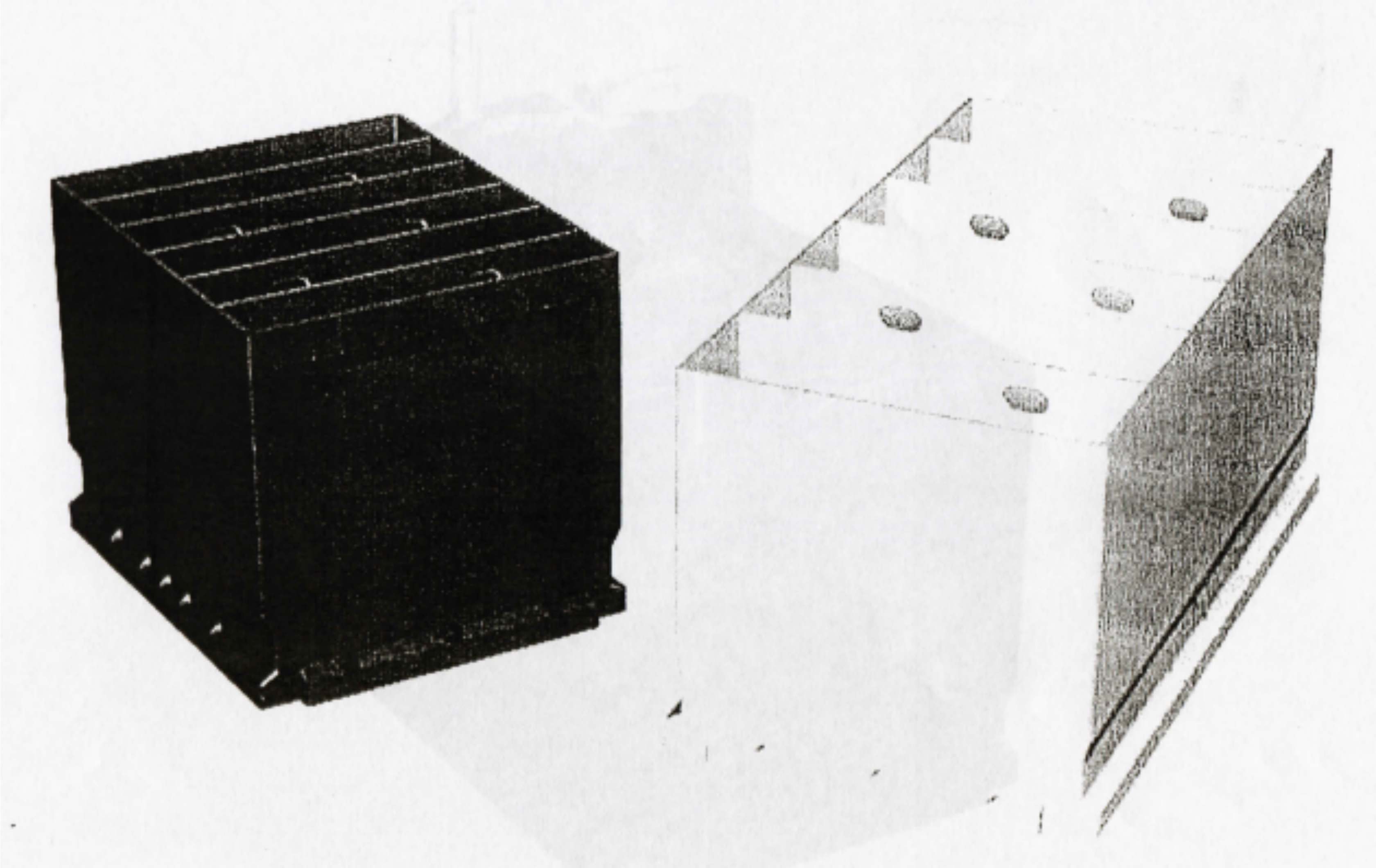
The lead-acid cell

Sealed, portable batteries



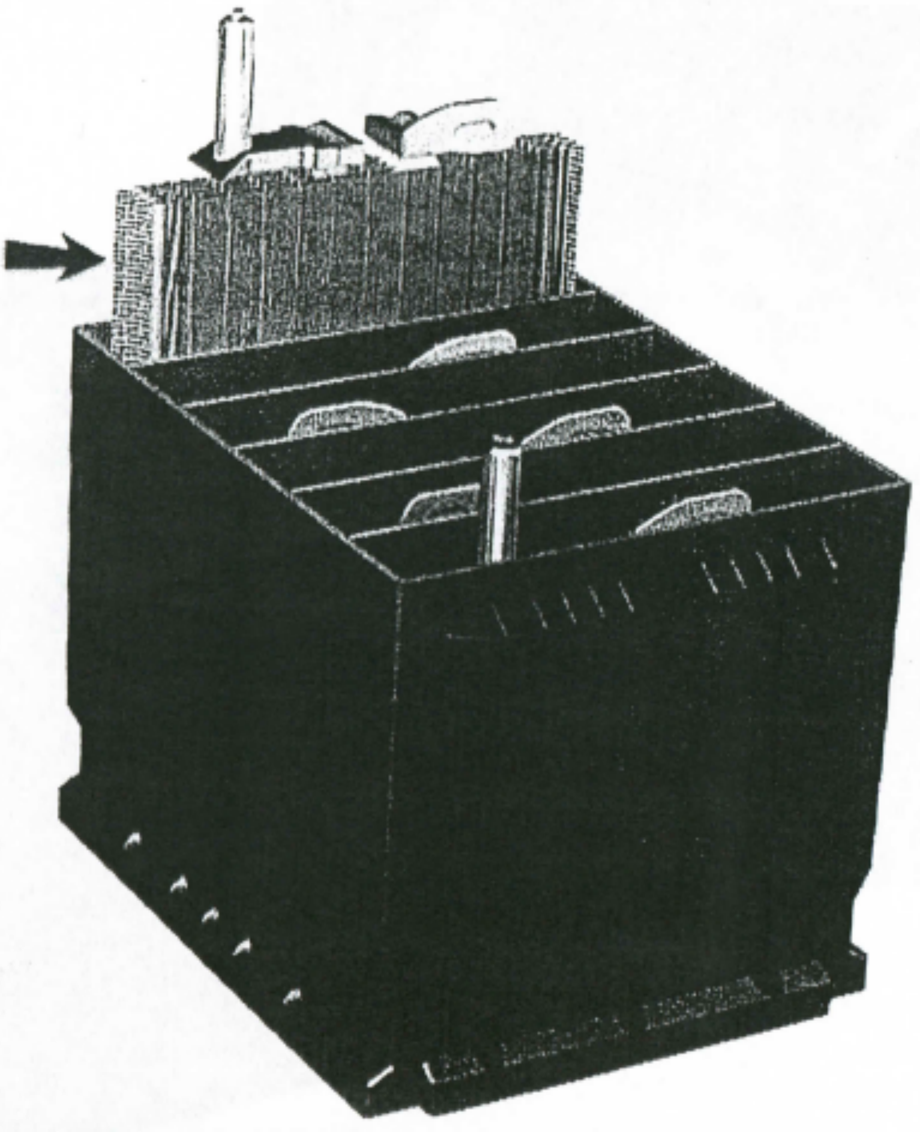
The lead-acid cell

Sealed, portable batteries



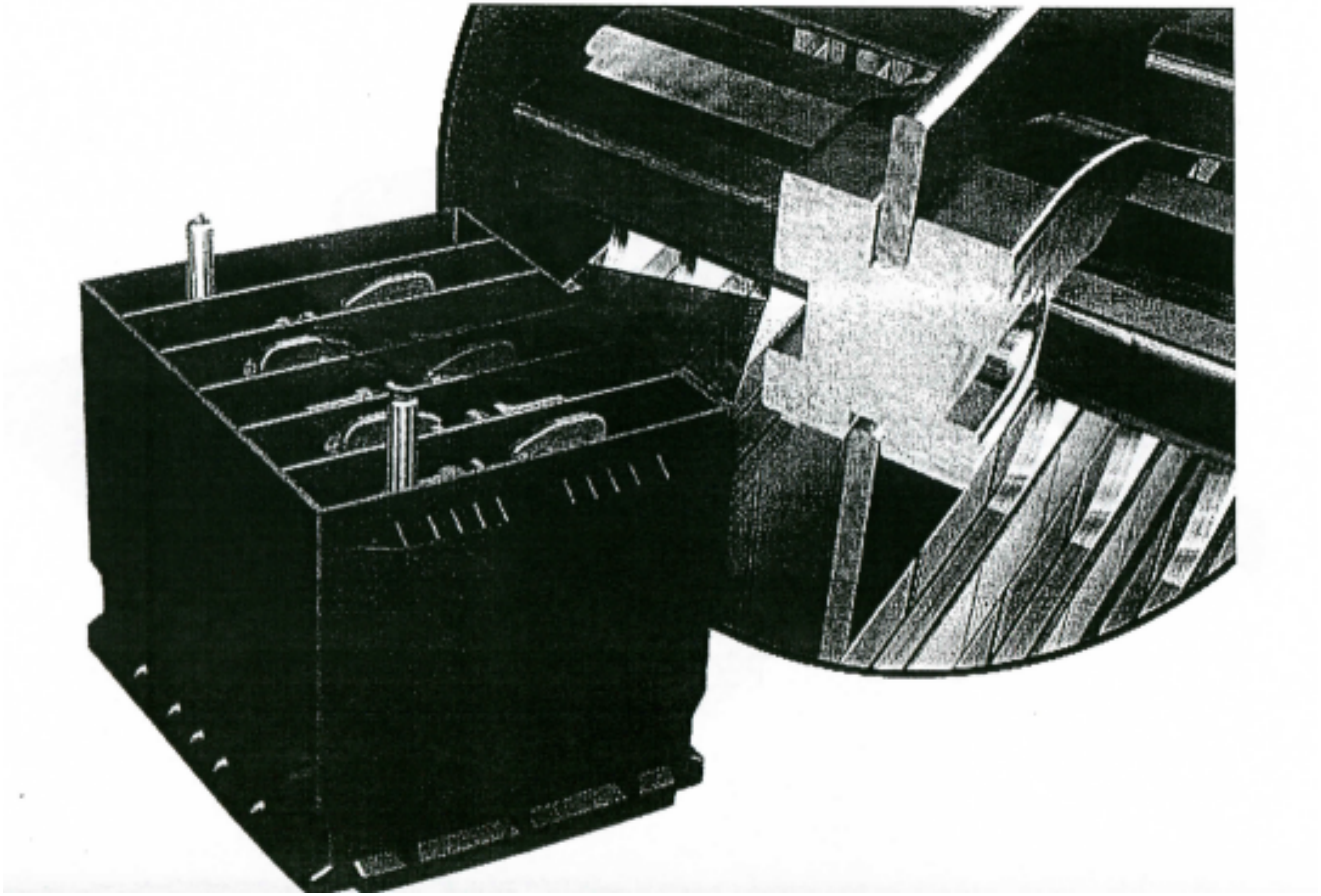
The lead-acid cell

Sealed, portable batteries



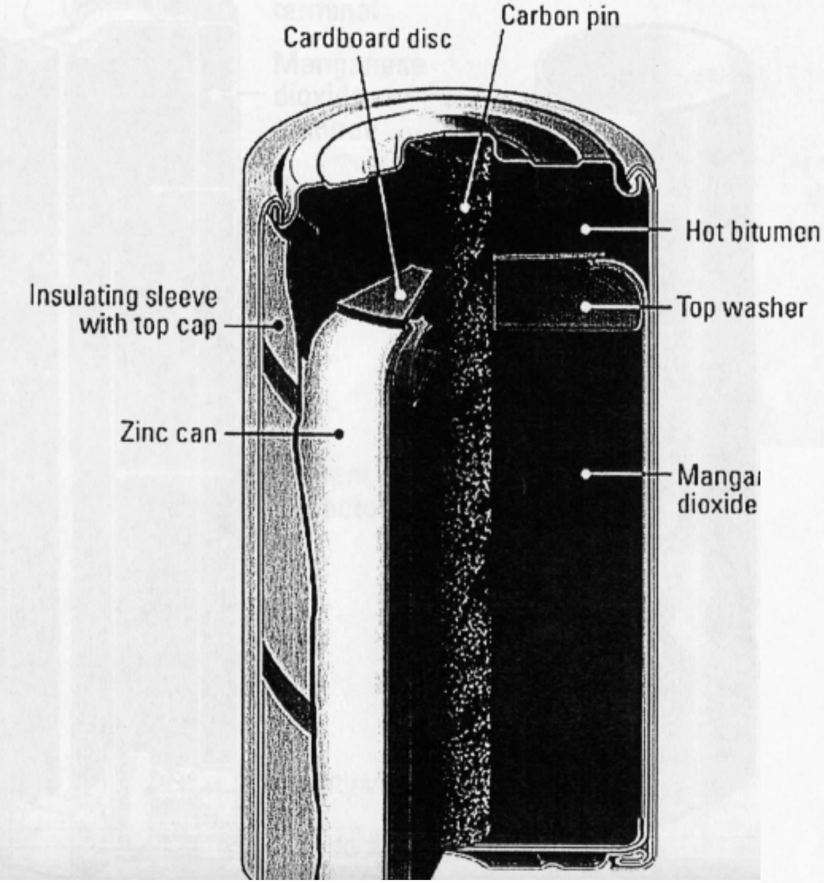
The lead-acid cell

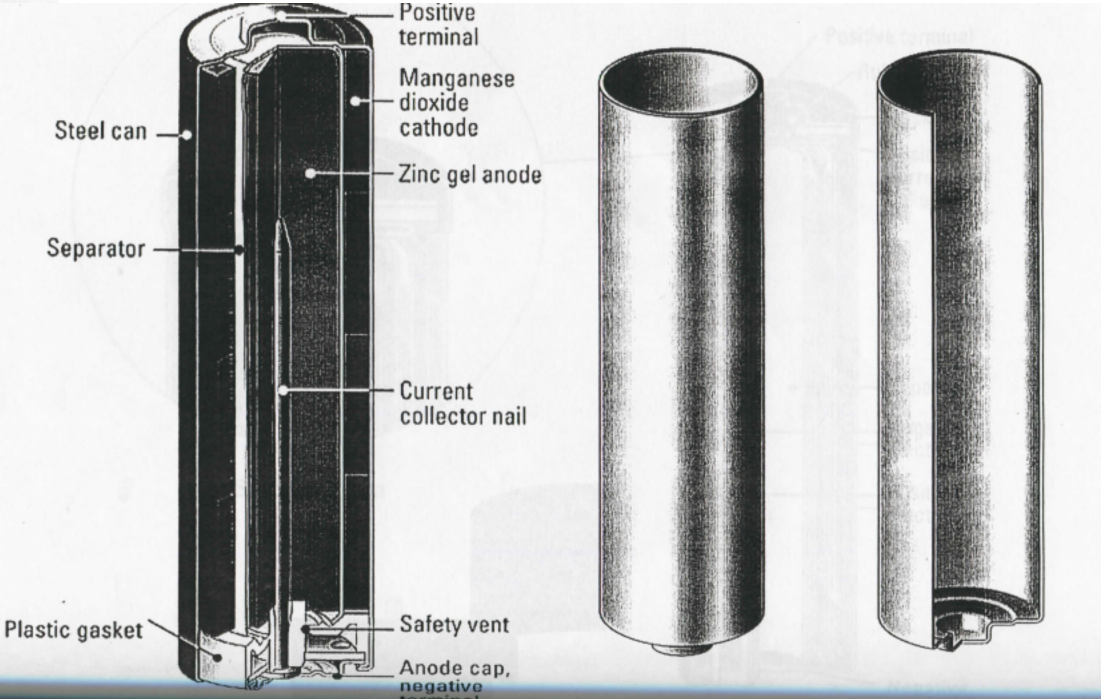
Sealed, portable batteries



The lead-acid cell

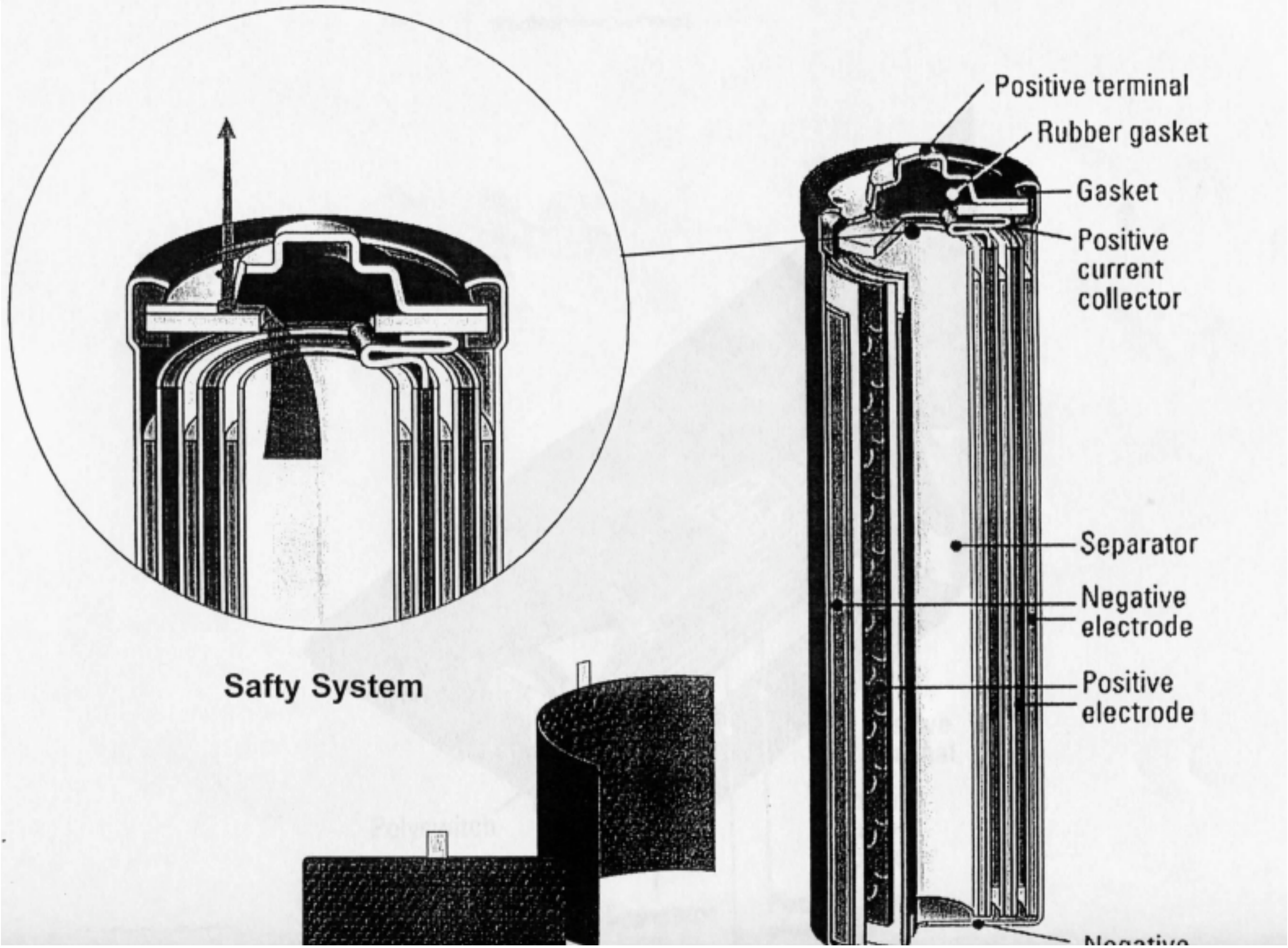
Sealed, portable batteries





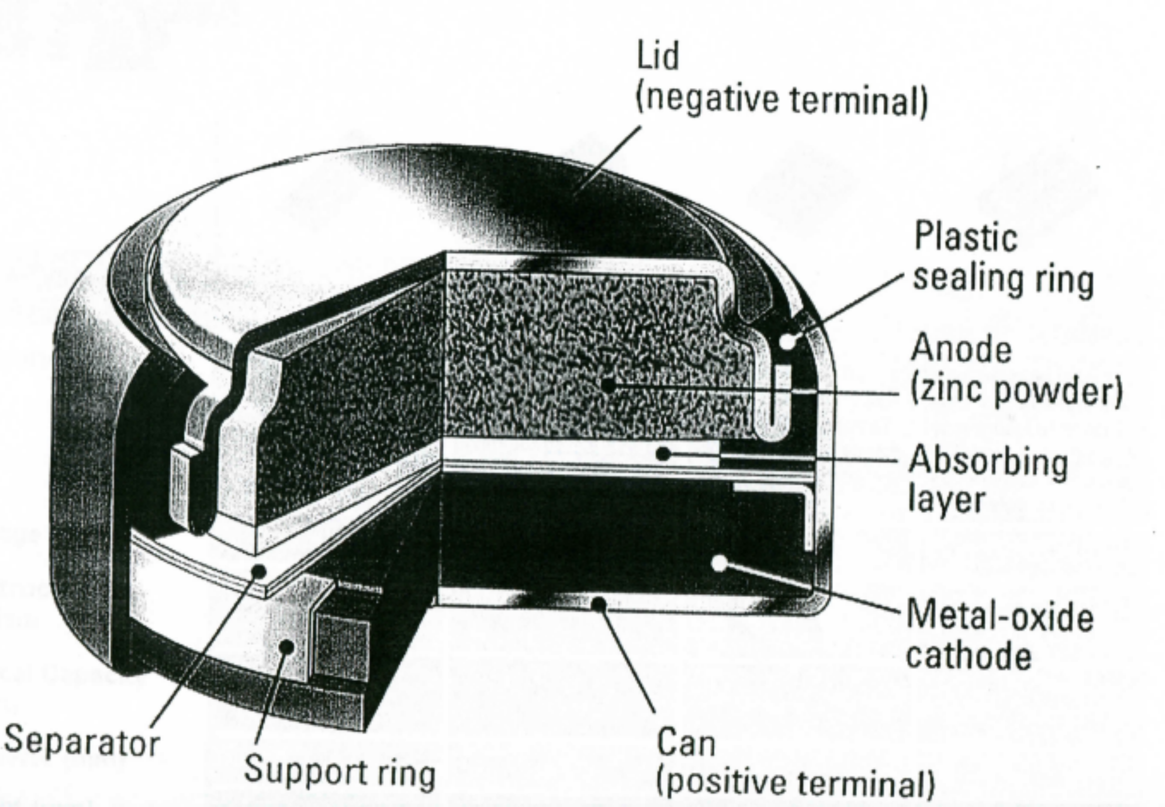
The lead-acid cell

Sealed, portable batteries

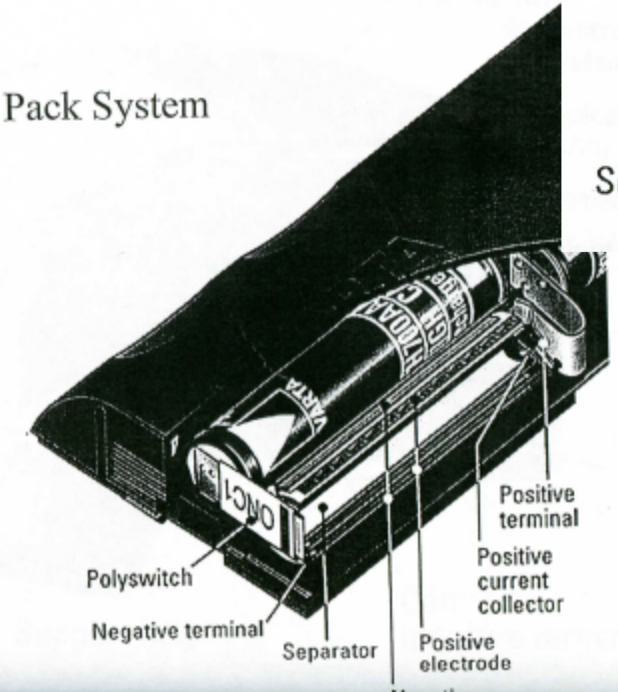


The lead-acid cell

Sealed, portable batteries



Power Pack System



The lead-acid cell

Sealed, portable batteries

Varta type Designation	T453	T455	T456	457
Voltage / V	6	7.2	3.6	3.6
Electrochemical system	Nichel Hydride	Li-ion	Li-ion	Nichel Hydride
Typical capacity / mAh	700	1350	1000	700
Diameter / mm	0	0	0	0
Height / mm	16.4	22.6	12	11.5
Weight / g	82	90	50	41

References: You are looking for the right Varta battery for your model of device?
With our device search you will easily find the suitable products

The lead-acid cell

Sealed, portable batteries

Varta type Designation	V384	V386	V389	V390
Voltage / V	1.55	1.55	1.55	1.55
Electrochemical system	Primar Silber	Primar Silber	Primar Silber	Primar Silber
Typical capacity / mAh	38	105	85	80
Diameter / mm	7.9	11.6	11.6	11.6
Height / mm	3.6	4.2	3.05	3.05
Weight / g	0.69	1.78	1.31	1.32
Reference IEC	SR41	SR43	SR54	SR54
Reference USA	-	-	-	-

The lead-acid cell

Sealed, portable batteries

Varta type Designation	5706	5906	CRAA	T399
Voltage / V	1.2	1.2	3	1.2
Electrochemical system	Nickel Hydride	Nickel Hydride	Primary lithiuk Zylindrisch	Nickel Hydride
Typical capacity / mAh	1600	1600	2000	1400
Length /mm	0	0	0	0
Width / mm	0	0	0	0
Height / mm	50.5	50.5	50.5	50.5
Diameter / mm	14.5	14.5	14.75	14.5
Weight / g	26	26	21.5	26
Type n°	5706	5906	6117	58399

The lead-acid cell

Sealed, portable batteries

Varta type Designation	4806	5006	5506	5606
Voltage / V	1.5	1.2	1.2	1.2
Electrochemical system	Primar Alkalisch Mangan	Nickel Cadmium	Nickel Hydride	Nickel Hydride
Typical capacity / mAh	2300	750	1100	1400
Length /mm	0	0	0	0
Width / mm	0	0	0	0
Height / mm	50.5	50.5	50.5	50.5
Diameter / mm	14.5	14.5	14.5	14.5
Weight / g	23	21	25	26
Type n°	4806	5006	5506	5606

The lead-acid cell

Sealed, portable batteries

Varta type Designation	3006	3706	4006	4706
Voltage / V	1.5	1.5	1.5	1.5
Electrochemical system	Zinck Chloride	Zinck Chloride	Primar Alkalisch Mangan	Primar Alkalisch Mangan
Typical capacity / mAh	1100	1200	2600	2600
Length /mm	0	0	0	0
Width / mm	0	0	0	0
Height / mm	50.5	50.5	50.5	50.5
Diameter / mm	14.5	14.5	14.5	14.5
Weight / g	21	21	23	23
Type n°	3006	3706	4006	4706