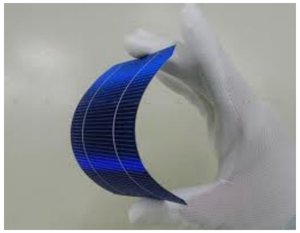
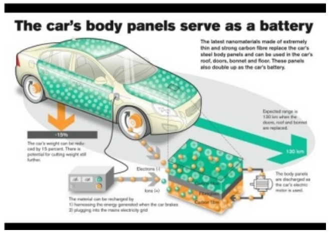
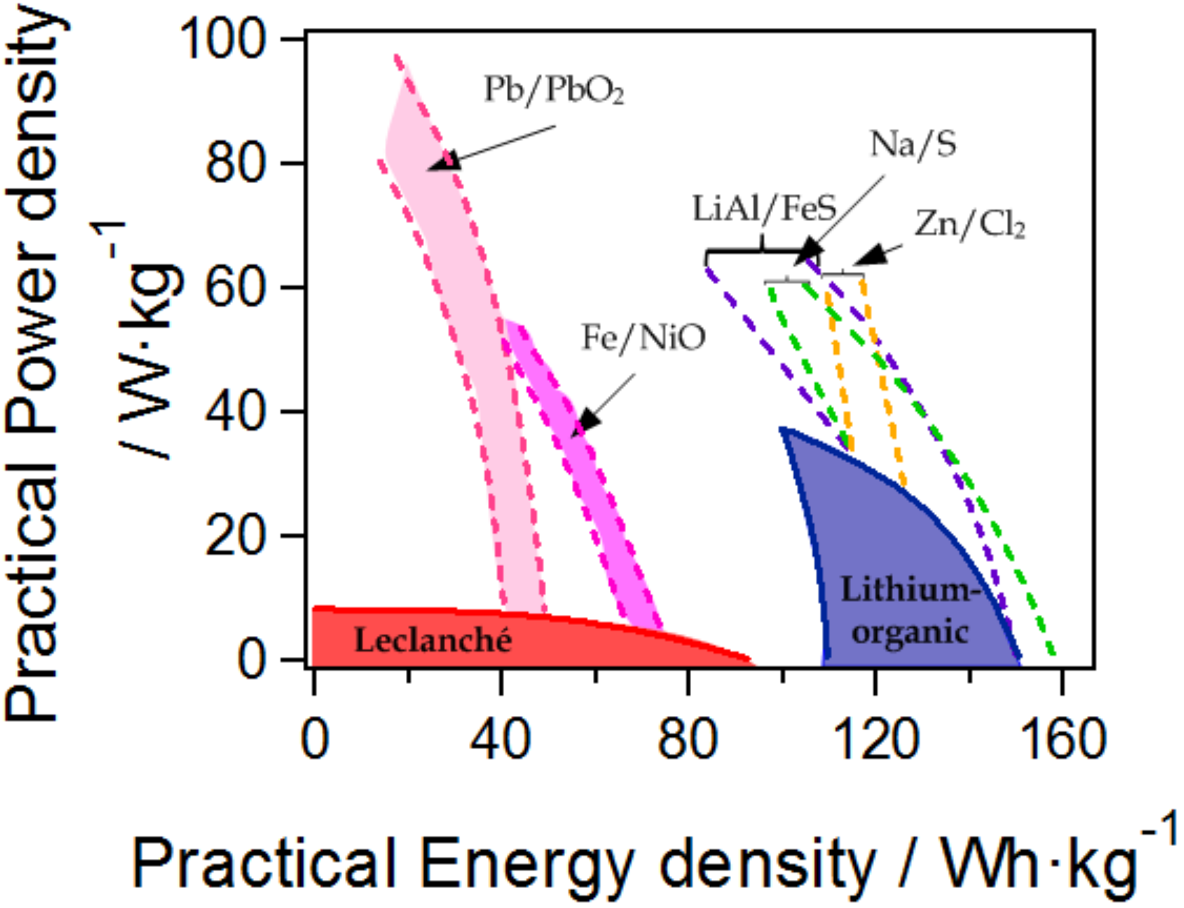
TECNOLOGIE PER L'ACCUMULO ELETTROCHIMICO

Prof. Vito Di Noto





Ambient lithium liquid electrolyte cells



Power density – energy density curves for practical battery system

Of all possible anode materials, **LITHIUM** is perhaps the most attractive since ***it combines a favorable thermodynamic electrode potential with a very high specific capacity*** (3.86 Ah·g^{-1}; 7.23 Ah·cm^{-3}).

As a result of its electropositive nature, Li rapidly reduces H_2O, and cells with Lithium anodes generally employ non-aqueous electrolytes.

Ambient lithium liquid electrolyte cells

The superior value of specific energy are evident.

Specific power is, however, limited, mainly because of the relative poor conductivity of the electrolytes. On the other hand, their low freezing point allows a lower working temperature than that for conventional aqueous batteries and the low chemical reactivity of lithium with these electrolyte leads to a satisfactory shelf life.

Lithium systems may be classified according to he physical state of the positive electroactive material:

- ✓ **Solid cathode reagents:** compounds with a negligibly small solubility in the electrolyte, e.g. CuO, FeS, etc…
- ✓ **Soluble cathode reagents:** the only important example is SO_2,
- ✓ **Liquid cathode reagents:** the active species in liquid form at the cell operating temperature, e.g. thionyl chloride, $SOCl_2$ and sulphuryl chloride, SO_2Cl_2.

Ambient lithium liquid electrolyte cells

The most commonly used solvents include cyclic esters (ethylene carbonate, propylene carbonate, γ-butyrolactone), linear esters, amide and sulphoxides

Properties of some solvents commonly used in lithium-organic cells (at 25°C unless otherwise state)

		MM	m.p. /°C	b.p. /°C	ε_r	μ / cP	ρ/g·cm^{-2}
Acetonitrile	AN	41.05	-45.7	81.6	38.0	0.345	0.79
γ-butyrolactone	BL	86.09	-42	206	39.1	1.750	1.13
1,2-dimethoxyethane	DME	90.12	-58	83	7.2	0.450	0.86
N,N-dimethylformamide	DMF	73.10	-61.0	149	36.7	0.796	0.95
Dymethylsulphoxide	DMSO	78.13	18.5	189	46.7	1.960	1.10
Dioxolane	DIOX	74.08	-95	78	--	--	1.06
Ethylene carbonate	EC	88.06	36.4	248	89.6*	1.850	1.32*

*** Determined at 40°C**

Ambient lithium liquid electrolyte cells

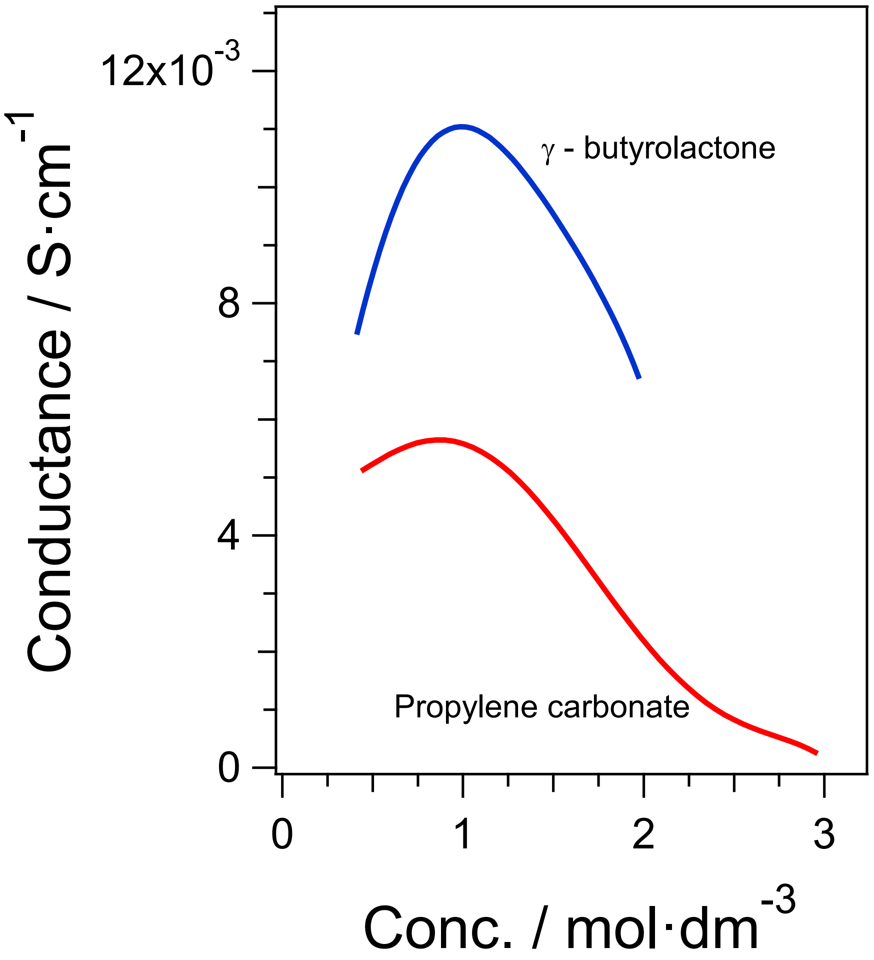
Properties of some solvents commonly used in lithium-organic cells (at 25°C unless otherwise state)

		MM	m.p. /°C	b.p. /°C	ε_r	μ / cP	ρ/g·cm^{-2}
Methyl formate	MF	60.05	-99.0	31.5	8.5*	0.340	0.97
2-methyltetrahydrofuran	MeTHF	86.12	-137.0	80	--	0.461	0.880
Nitromethane	NM	61.04	-28.5	101.0	35.9	0.620	1.14
Propylene carbonate	PC	103.09	-48.8	242	66.1	2.530	1.21
tetrahydrofuran	THF	72.12	-108.0	65.0	7.4	0.457	0.848

*** Determined at 20°C**

A **mixed** solvent is sometimes preferred since the properties of the electrolyte solution (conductance, viscosity, etc…) and its reactivity towards lithium can often be ‘tailored’ to give optimum performance. The most widely used salts are $LiClO_4$, $LiAlCl_4$, $LiBF_4$ and $LiAsF_6$, i.e either simple salts or combinations of a lithium halide with a Lewis acid.

Ambient lithium liquid electrolyte cells



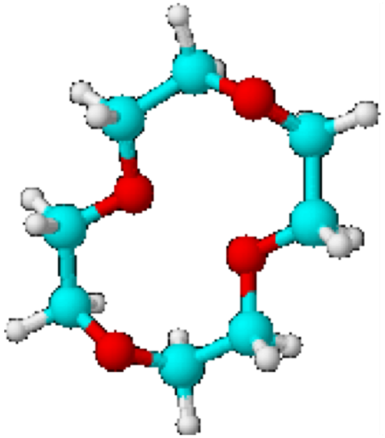
Conductance of LiAsF6 in γ-butyrolactone and propylene carbonate as function of the concentration (by permission of the Electrochemical Society)

The conductance of lithium salt solutions in aprotic solvents generally shows a maximum as the concentration of electrolyte is increased.

Such maxima can be interpreted on the basis of the opposing influence of:

- ✓ an increasing number of charge carriers on the one hand,
- ✓ an increasing viscosity and increasing ion association with the formation of non-conducting ion pairs, on the other.

Ambient lithium liquid electrolyte cells



It has been shown that the conductance can be increased by the addition of crown ethers, such as

12-crown-4.

This can be attributed to a decrease in ion-association due to shielding of the charge on the lithium ions.

Highest values of conductance of some $LiClO_4$ solutions at 25°C

Solvent	Conc. mol·dm^{-3}	Conductance S·m^{-1}
Dimethylformamide	1.16	2.22
Dimethylsulphoxide	1.5	1.0
Methyl formate	2.8	3.20

LiAsF6 is pre-eminent as a solute, particularly for rechargeable systems, because of its favorable stability, solubility and conductance

Ambient lithium liquid electrolyte cells

Maximum solubility of $LiAsF_6$ at 25°C

Solvent	**Concentration mol·dm^{-3}**
Acetonitrile	1.60
Dimethylformamide	4.68
Propylene carbonate	4.66
Water	3.28

In methyl formate (MF), $LiAsF_6$ dissolves to give one of the most conductive organic electrolyte solutions known: at 25°C a solution of 2mol·dm^{-3} has a conductance of 4.5 S·m^{-1}.
while this combination can be considered as a suitable electrolyte for 'high rate' cells, its suffers from some deposition with gassing in the presence of lithium unless stabilized with materials such as $(CH_3)_4NBF_4$.

Ambient lithium liquid electrolyte cells

Conductivity of some LiAlCl4 solutions in organic solvents at 25°C

Solvent	Concentration mol·dm^{-3}	Conductance S·m^{-1}
Dimethylformamide	1.16	2.22
Dimethylsulphoxide	1.5	1.0
Methyl formate	2.8	3.20

$LiAlCl_4$ is the solute which is most widely used to increase the conductance of inorganic liquid cathode materials such as $SOCl_2$ and SO_2Cl_2.

The solvent used in lithium batteries are generally thermodynamically unstable in the presence of lithium: the low lithium corrosion rate and consequent good shelf life actually experienced with sealed cells is due to the formation of a protective film on the surface of the metal.

The practical stability of the electrolyte solutions in the presence of lithium depends on their purity and in particular, on low water content.

A number of procedures have been proposed for the purification and drying of solvents, including operations such as pre-electrolysis with platinum electrodes.

Ambient lithium liquid electrolyte cells

Oxidation potentials of some inorganic salt/ether solvent systems

Solvent	Salt	Concentration mol·dm^{-3}	Oxidation potential vs Li^+/Li
Dioxolane	$LiClO_4$	2.0	3.4
	$LiPF_6$	1.0	3.50
	$LiAsF_6$	1.5	3.60
Dioxolane + 0.1mol·dm^{-3} pyridine	$LiAsF_6$	1.5	3.84
2-methyltetrahydrofuran	$LiAsF_6$	1.0	4.32
4-methyltetrahydrofuran	$LiAsF_6$	1.0	3.32

Room temperature: platinum substrate; current density 1mA·cm^{-2}. (H.H. Horowitz et al., Fall Meeting of the Electrochemical Society, Hollywood, Florida, 1980. extended Volume 80-82 (1980) p. 177). Reprinted by permission of the publisher, The Electrochemical Society, Inc.

The electrochemical stability of a solution can be defined as the voltage range within which it does not undergo detectable electrolytic decomposition, for a particular pair of electrodes. In the case of a practical primary cell such a range must be wider than the OCV.

Ambient lithium liquid electrolyte cells

THE LITHIUM ANODE IN PRIMARY CELLS:

Film formation of lithium

Physical properties of Lithium	
Atomic weigh	6.94
Melting point	180.5 °C
Boiling point	134.7 °C
Density	0.534 g·cm^{-1} at 20°C
Heat of fusion	3.001 kJ·mol^{-1}
Heat of evaporation	147.1 kJ·mol^{-1}
Resistivity	$9.446\times10^{-6}\Omega$·cm at 20°C

The reaction of lithium with the electrolyte to form a surface film significantly modifies its behavior. On the one hand the film confers chemical stability and useful shelf-life on the system.

On the other, it is responsible for greatly depressed exchange currents and the consequent phenomenon of voltage delay.

It is convenient to discuss separately film formation with:

a) Insoluble

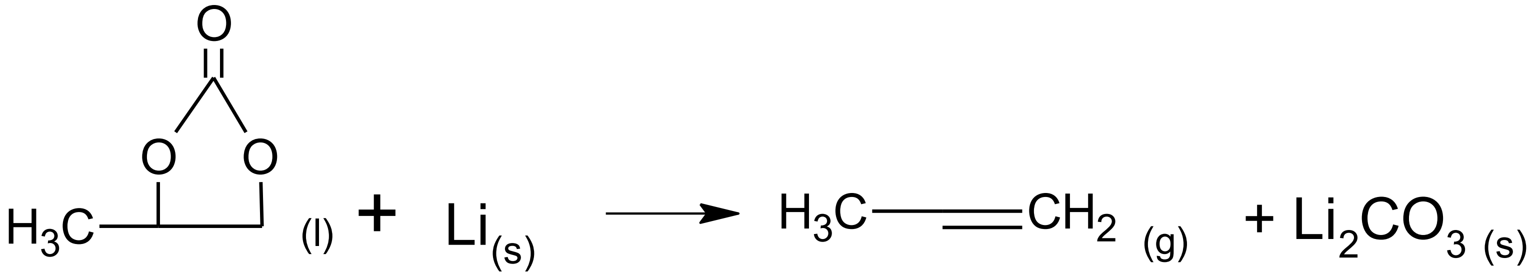
b) Liquid and soluble cathode systems.

Ambient lithium liquid electrolyte cells

CELLS WITH INSOLUBLE CATHODIC REAGENTS

In these cells, provided that the solubility of the cathode material is very low, the solvent itself is principally responsible for film formation.

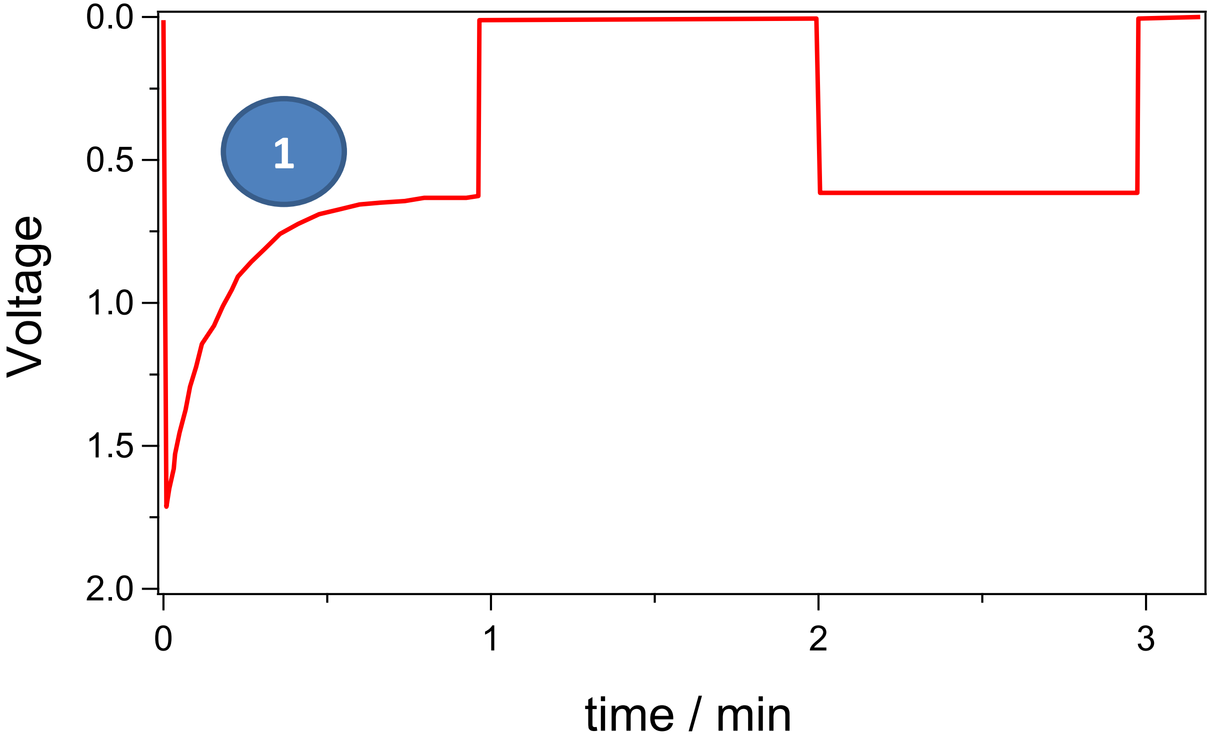
The most detailed studies have been performed on PC-based electrolytes where the thermodynamically favored reaction is:



Propene evolution has been observed on lithium amalgams and also at platinum surfaces connected to lithium electrodes. with solid lithium itself, however, a lithium carbonate film is immediately formed which passivates the metal surface. The level of trace impurities, such as water, does not affect the film formation significantly. Passive films have also been observed on lithium in solvents such as BL, DME, AN, MF, THF, etc…

Ambient lithium liquid electrolyte cells

CELLS WITH INSOLUBLE CATHODIC REAGENTS

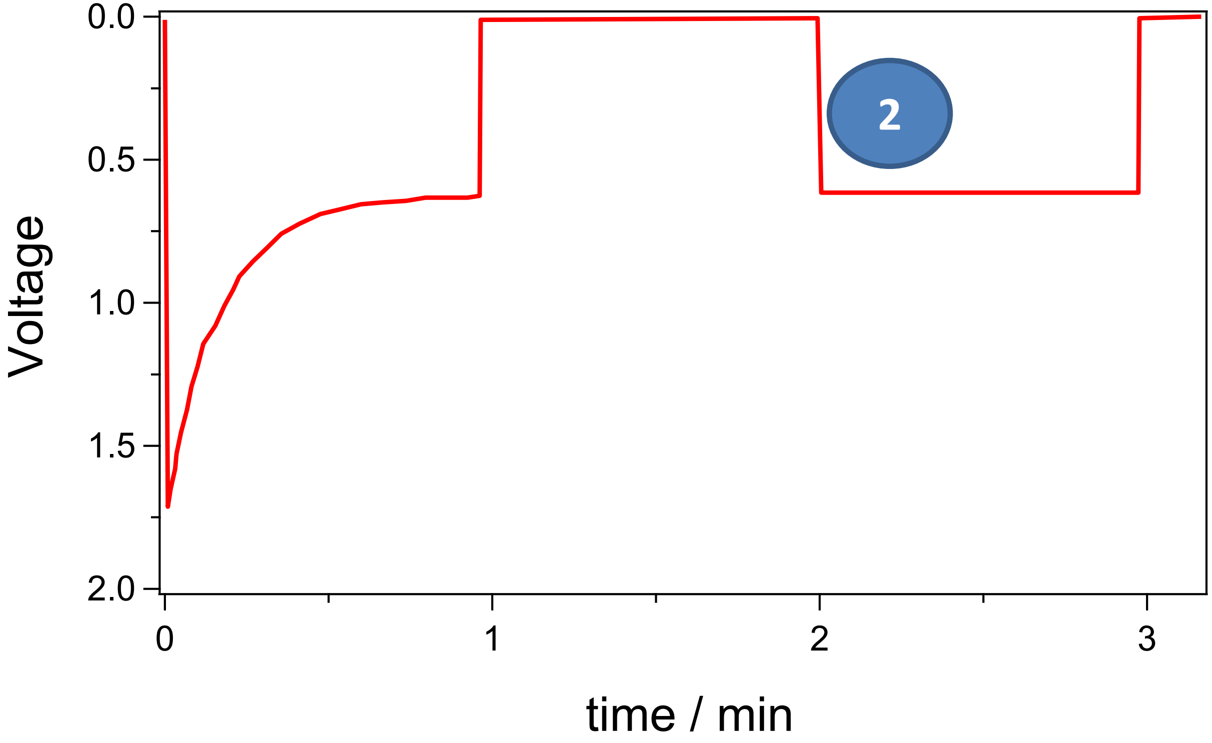


Voltage recovery of a Li anode at -20°C in 1mol·dm^{-3} LiClO$_4$ in PC vs Li reference electrode. current density: 10mA·cm^{-2}.

① On drawing current from a passivated lithium anode, polarization is at first severe, but the voltage recovers fairly rapidly. Initially, the charge transfer process at the anode is mainly lithium dissolution through imperfections in the film. This dissolution progressively disrupts and removes the film, thus allowing the discharge voltage to rise rapidly to its steady value.

Ambient lithium liquid electrolyte cells

CELLS WITH INSOLUBLE CATHODIC REAGENTS



Voltage recovery of a Li anode at -20°C in 1mol·dm^{-3} LiClO$_4$ in PC vs Li reference electrode. current density: 10mA·cm^{-2}.

2 If the cell is now returned to open circuit, and a second current pulse is subsequently withdrawn, no voltage delay is observed if the period on open circuit is too brief for reformation of the film. In commercial lithium batteries of this type, recovery from voltage delay is very rapid under normal working conditions, but is slower at low temperatures.

Ambient lithium liquid electrolyte cells

CELLS WITH LIQUID OR SOLUBLE CATHODIC REAGENTS

The formation of passivating films on lithium in contact with liquid or soluble cathodic reagents is a pre-requisite for the construction of a practical cell. The film acts in the same way as a separator, preventing further direct chemical reaction of lithium and the cathodic reagent. However film formation involving the action of SO_2, $SOCl_2$, etc… on lithium is considerably more complex, and may produce more severe voltage delay characteristics than in the case of insoluble cathodes described above.

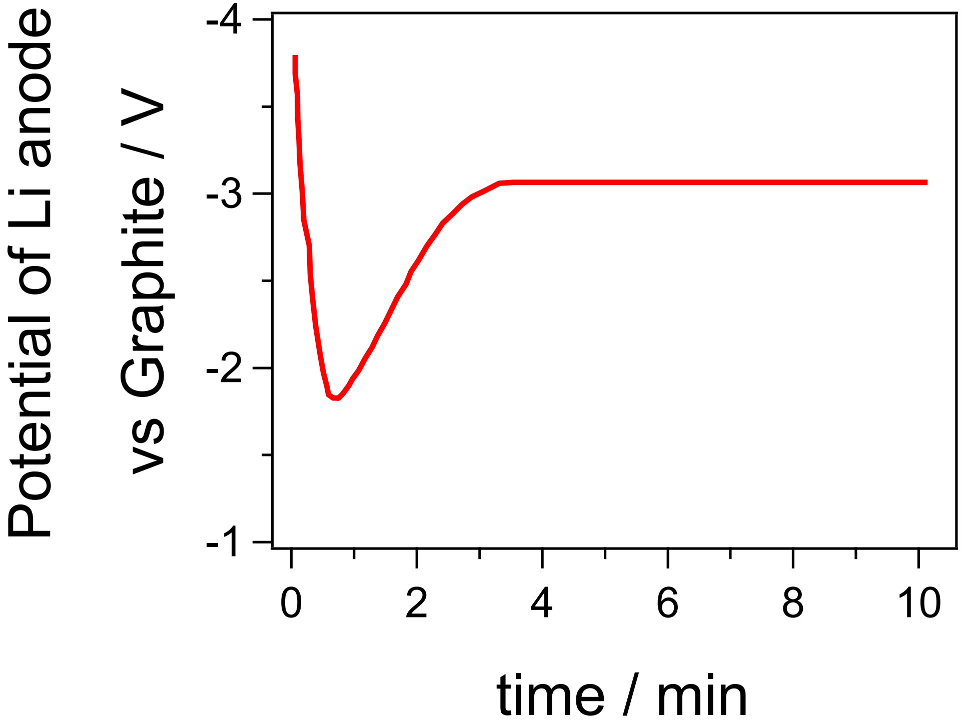
When SO_2 dissolved in AN is brought into contact with lithium, a layer of lithium dithionite is formed, following the same reaction scheme ad the normal cell reaction:

$$2Li_{(s)} + 2SO_{2,(diss.)} \rightarrow Li_2S_2O_{4,(s)}$$

Ambient lithium liquid electrolyte cells

CELLS WITH LIQUID OR SOLUBLE CATHODIC REAGENTS

If the solvent is a PC/AN mixture, the film constitution is complex and contains Li_2CO_3 in addition to $Li_2S_2O_4$. This latter film is probably more coherent or compact since the voltage delay is greater than for the pure dithionite film. With $SOCl_2$ and SO_2Cl_2 containing $LiAlCl_4$ a particularly severe voltage delay is observed especially after prolonged storage.

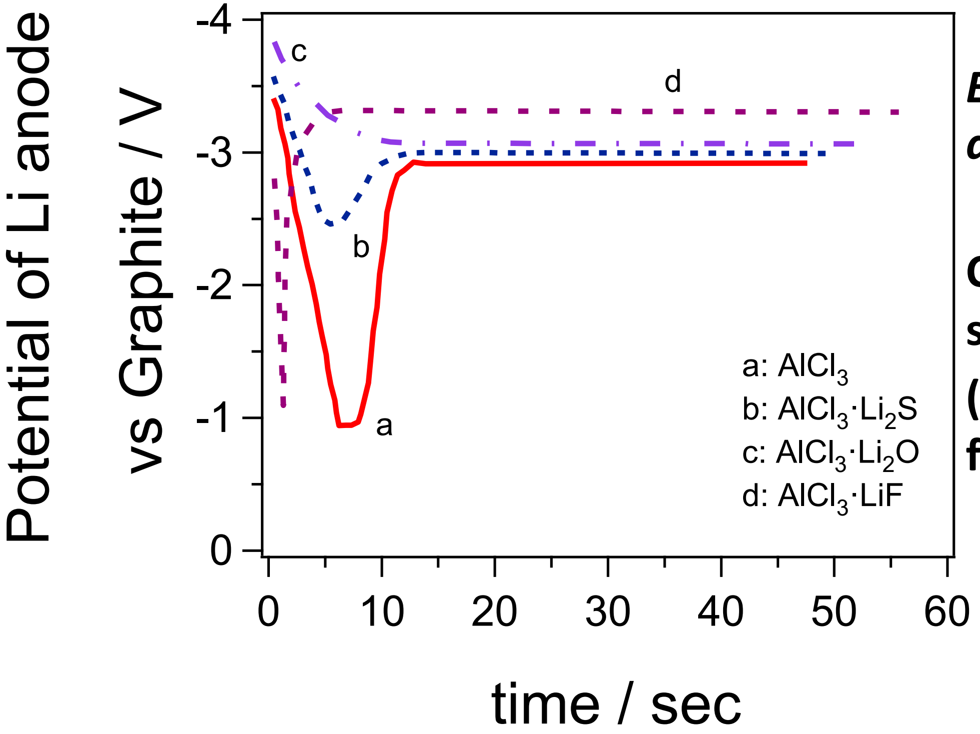


Initial discharge behavior of a $Li_{(s)}|LiAlCl_4,SO_2Cl_2(l)|C(s)$ cell after prolonged storage at room temperature.

Current density at Li electrode: 5 mA·cm^{-2}

Ambient lithium liquid electrolyte cells

CELLS WITH LIQUID OR SOLUBLE CATHODIC REAGENTS



Effect of electrolyte composition on discharge behavior of

$Li_{(s)}|$(electrolye, 1mol·dm^{-3}),$SO_2Cl_2(l)|C(s)$.
Current density at Li electrode: 6.4mA·cm^{-2}.
storage: 15 days at 25°C or 7 days at 70°C

(by permission of the International Society for Electrochemisty)

The film consists primarily of LiCl crystals whose growth and morphology follow a complex pattern and are affected substantially by additives such as $AlCl_3$, S_2Cl_2, H_2O, and by other electrolyte variables. A number of investigators have recently shown how film growth in these systems can be controlled and voltage delay reduced, by careful selection of electrolyte components. The advantage of neutralizing the acidic AlCl3 with stronger Lewis bases, i.e. Li_2O rather LiCl, has been shown.

Ambient lithium liquid electrolyte cells

CELLS WITH LIQUID OR SOLUBLE CATHODIC REAGENTS

In practical terms, the twin objectives of protecting the lithium from corrosion while avoiding unacceptable levels of voltage delay can be considered to have been met.

However the detailed mechanisms of film formation and disruption are still matters of some controversy.

In particular the interaction of thin films formed rapidly on lithium surface exposed to the atmosphere with the thicker films formed by subsequent reaction with the cathodic reagent, is not ell understood.

Ambient lithium liquid electrolyte cells

CATHODE MATERIALS AND LITHIUM PRIMARY CELLS

Lithium primary cells can be divided into three categories depending on the type of cathode used:

a) In the first group, the cathodic reagent is a solid material, almost insoluble in the electrolyte,

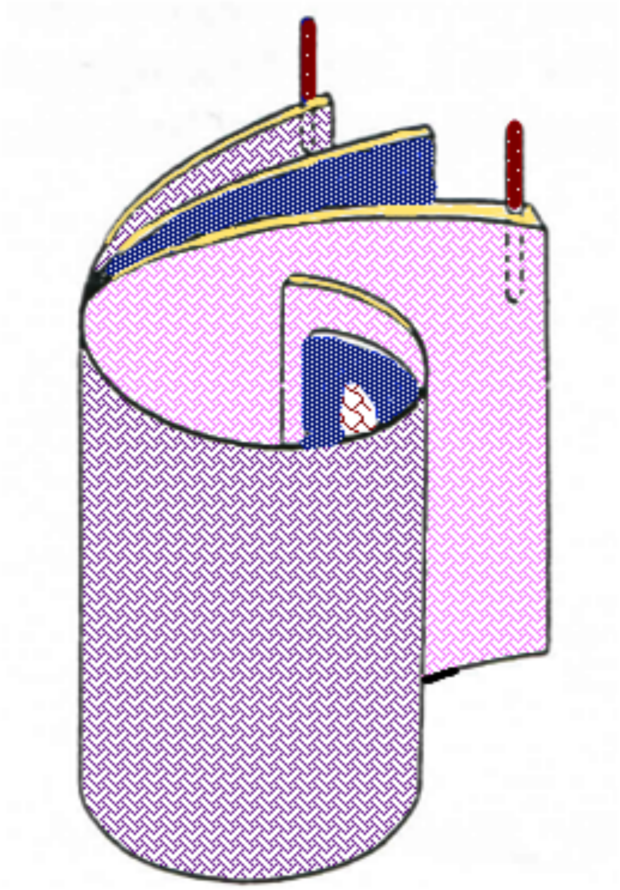
b) In the second, it is completely dissolved in the electrolyte;

c) In the third, it is a liquid, and in addition to being the species responsible for uptake of electrons from the external circuit, it acts as solvent for the supporting electrolyte which carrier the current through the cell.

Most of the commercial cells currently on the market belong to the first group, although there are examples in the other two categories.

Ambient lithium liquid electrolyte cells

CATHODE MATERIALS AND LITHIUM PRIMARY CELLS



Spiral wound battery construction

The cells are manufactured in a number of forms of which the standard button cell is the most important. When cells with higher capacities are required, a spiral wound design is preferred. bobbin-type cells are use to achieved higher energy density.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM

Four main group of compounds may be distinguished: polycarbon fluorides, oxosalts, oxides and sulphides.

Polycarbon fluorides

The coupling of lithium with free halogens gives rise to cells of exceptionally high specific energy. Unfortunately, the chemical reactivity of the components is generally too high.

the solid state lithium-iodine cell is however a commercial success, and prototype solid state lithium-bromine cells have been successfully tested. In the case of fluorine the problem has been overcome by effectively immobilizing the fluorine in a graphite host.

Polycarbon fluorides, of general formula $(CF_x)_n$ can be obtained by direct fluorination of carbon black, or other carbon varieties at high T.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Polycarbon fluorides**

For fluorine compositions in the range $0.4<x<1.0$, such substances have very high specific energies (e.g., 2600 Wh·kg^{-1} for $x = 1$).

For $x < 1$ the materials are electronic conductors. Lithium cells with polycarbon fluoride cathodes have OCV value in the range of 2.8 – 3.3 V, depending on the exact formulation of the cathode material.

A typical cell may be written as:

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with associated cell reaction

$$nxLi_{(s)} + (CF_x)_{n,(s)} \rightarrow nC_{(s)} + nxLiF_{(diss)}$$

It is believed that the discharge mechanism involves the formation of an intermediate lithium ‘intercalation’ compound in which both Li and F are situated between the carbon layers of the graphitic structure.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Polycarbon fluorides**

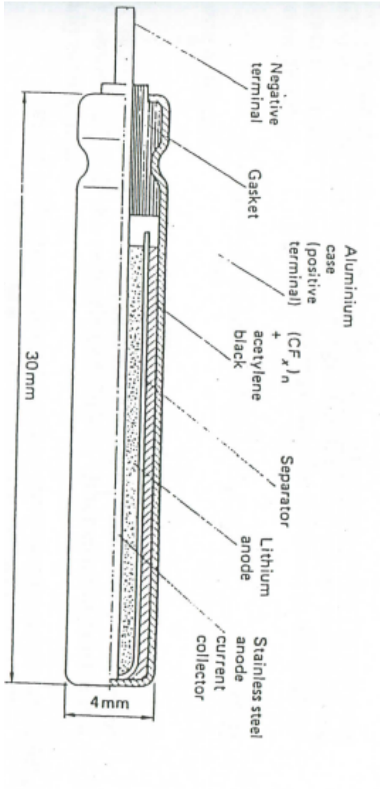
The $(CF_x)_n$ cathode is stable in contact with organic electrolyte systems, and the cells have a satisfactory shelf life. In common with other lithium power sources, polycarbon fluoride-based cells suffer from voltage delay. However in these cells the effect may be more severe due to additional contribution from the cathode. At high fluorine contents, $(CF_x)_n$ has a high electronic resistance which falls only as x is reduced during cell discharge.

Cells based on polycarbon fluorides are manufactured commercially in a number of forms. The system was developed first by Matsushita Electrical Industrial Co. in Japan, and cells for military applications have been produced in USA by Eagle Picher and Yardney Electric. The spiral wound cylindrical cells have the largest capacity and are used in portable radio transceivers, surveying cathode and a central lithium anode, all enclosed in a light aluminum case.

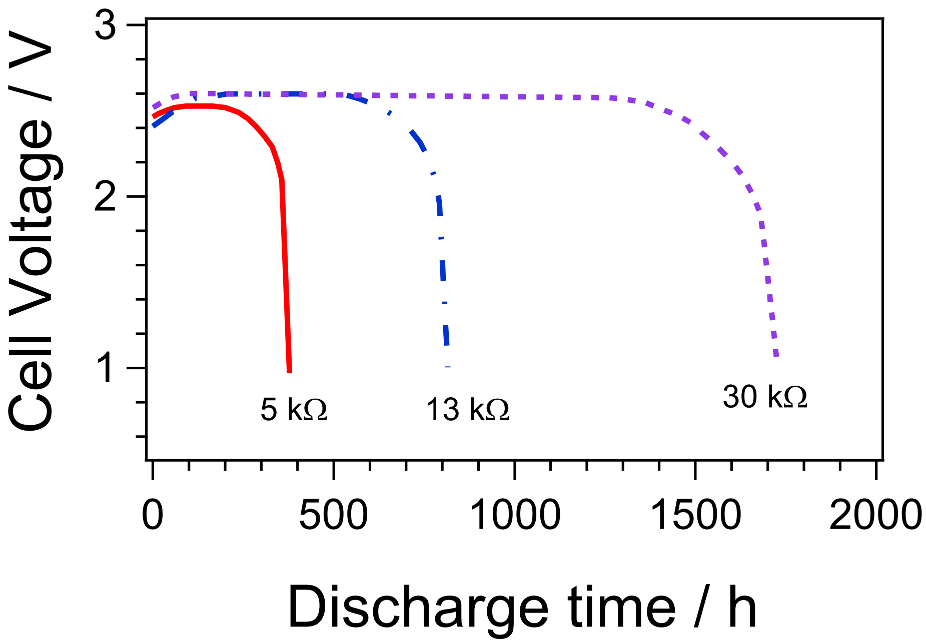
Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM

Polycarbon fluorides



Lithium-$(CF_x)_n$ cylindrical cell (based on the design of Matsushita (BR435), by permission)



Discharge curves of Lithium-$(CF_x)_n$ button cells under various loads at ambient temperature (by permission of Elsevier Sequoia, S.A.)

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM

Polycarbon fluorides

Specifications of some commercial Li-($(CF_x)_n$) cells

(National Matsushita Electrical Industrial Co., Japan)

	Button	Inside-out	Spiral
OCV	3.0	3.0	3.0
Nominal capactity / mAh	150	40	5000
Energy density / Wh·kg^{-1}	140	140	320
Diameter / mm	23	4.2	26
Height / mm	2.5	35.9	50
Weight / g	3.1	0.85	47.0

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Oxosalts**

Silver, copper and other oxosalts have been extensively studied as cathodes in laboratory cells and there is a range of commercial power sources based on silver chromate.

The main discharge process for lithium cells based on the latter material is

$$2Li_{(s)} + Ag_2CrO_{4,(s)} \rightarrow 2Ag_{(s)} + Li_2CrO_{4,(s)}$$

for which the cell

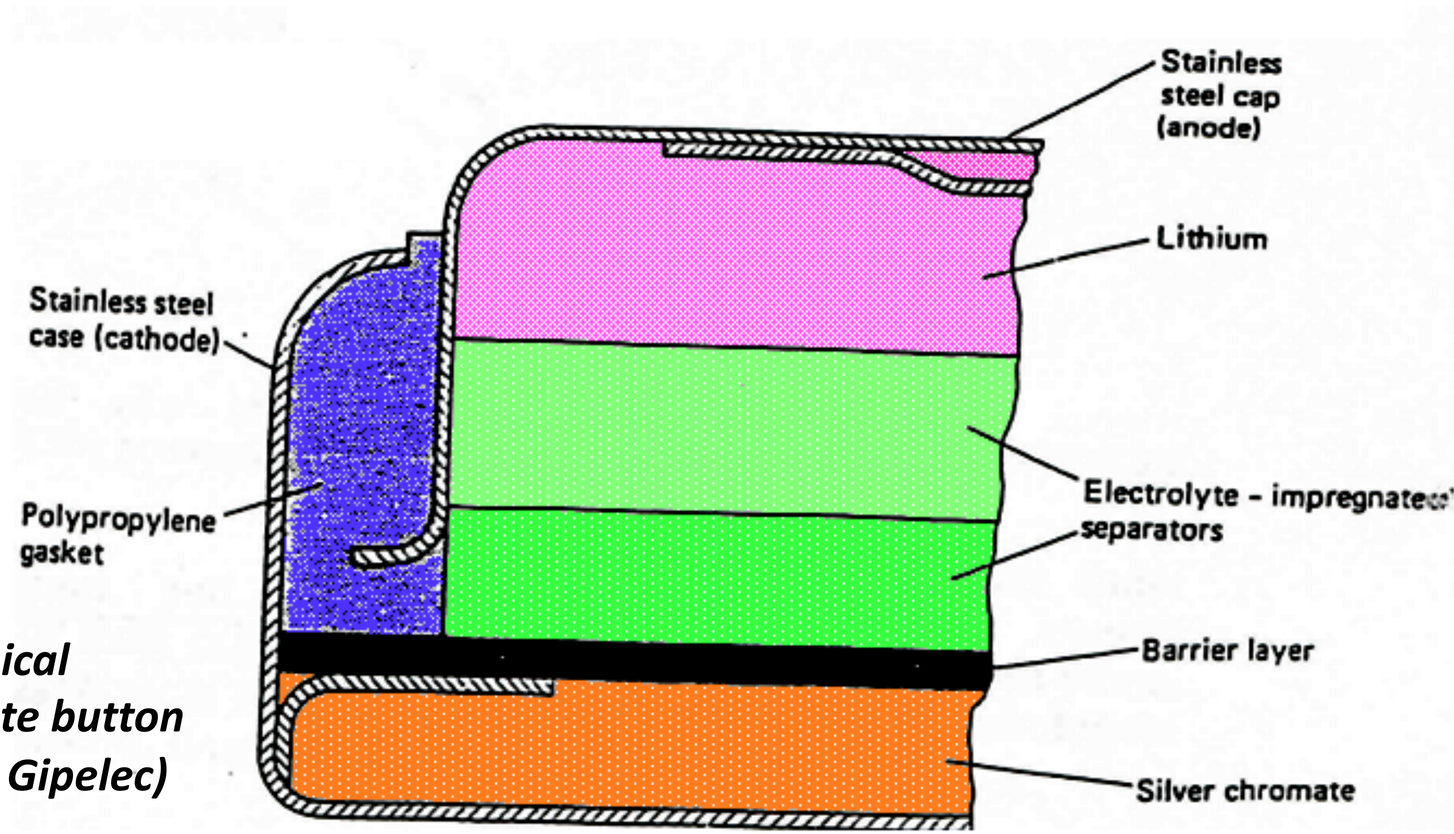
$$Li_{(s)}|LiClO_4, PC|Ag_2CrO_{4,(s)}, C_{(s)}$$

has a nominal OCV of 3.5 V. A secondary reduction process follows at about 2.5 V, associated with the reduction of Cr(VI). Other oxosalts behave in a broadly similar manner.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Oxosalts**

Silver chromate-based cells are manufactured in button and rectangular (prismatic) form in a number of sizes. The energy density of such complete systems is estimated as 200 W·kg^{-1} or 575 Wh·dm^{-3}, to a 2.5 V cut off.



Cross-section of a typical lithium-silver chromate button cell (courtesy of SAFT Gipelec)

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM

Oxosalts

Specifications of some commercial Li-Ag_2CrO_4 button cells (SAFT Gipelec)

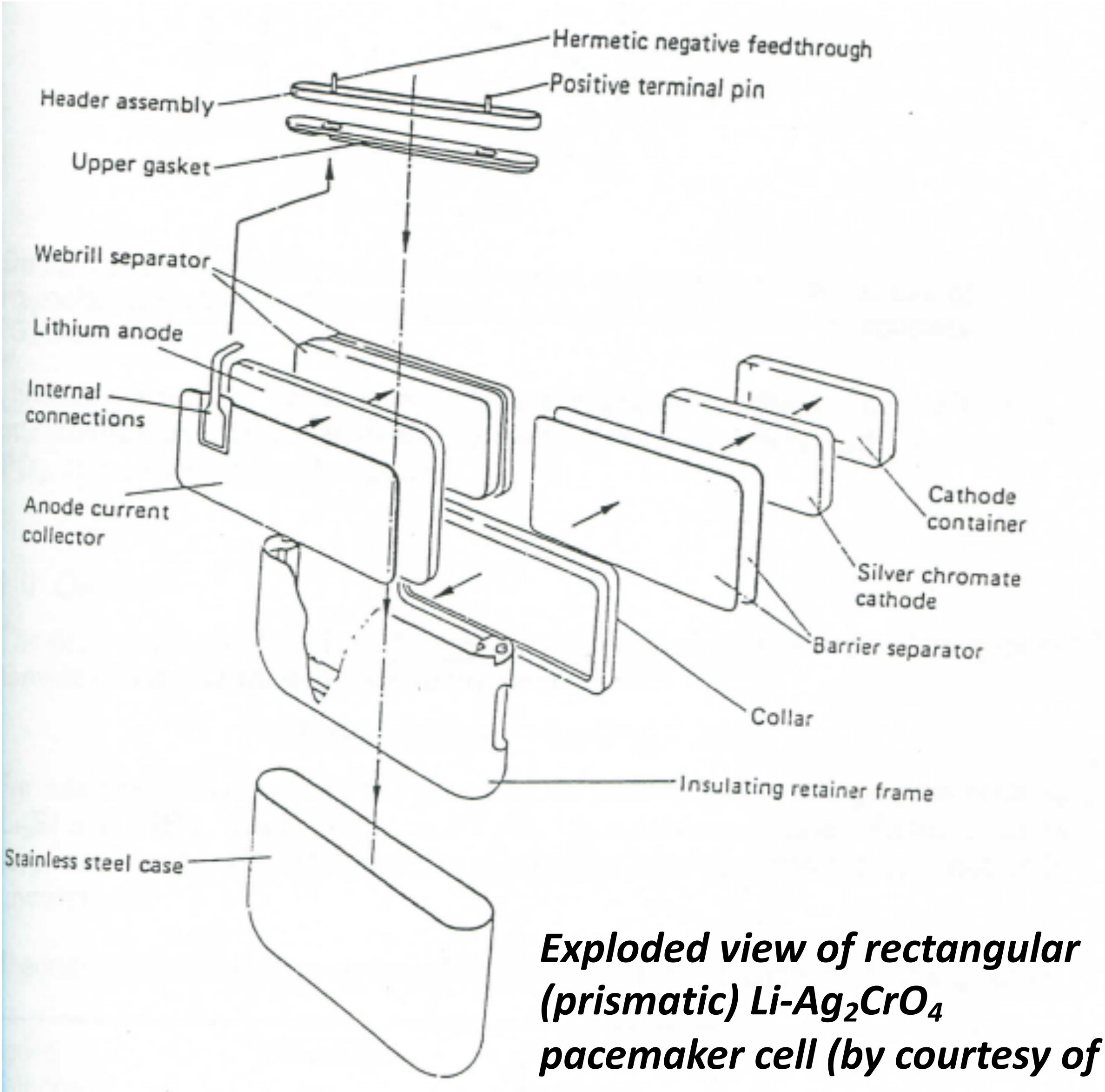
OCV	3.5	3.5	3.5	3.5	3.5	3.5
Nominal capacity / mAh	90	600	900	1310	1750	2300
Practical capacity at 2.7 V cut-off / mAh	86	540	810	1180	1570	2070
Diameter / mm	11.4	21.0	27.3	35.5	35.5	35.5
Height / mm	5.4	9.1	7.9	6.0	8.0	10.0
Weight / g	1.7	8.9	12.5	17.0	22.5	29.0

The excellent reliability under continuous drain, and the low self-discharge (1% per annum) characteristic of these cells have made them one of the commonest power supplies for pacemakers and other implanted devices such as neurological pain-relieving systems, drug dispensers, etc…

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM

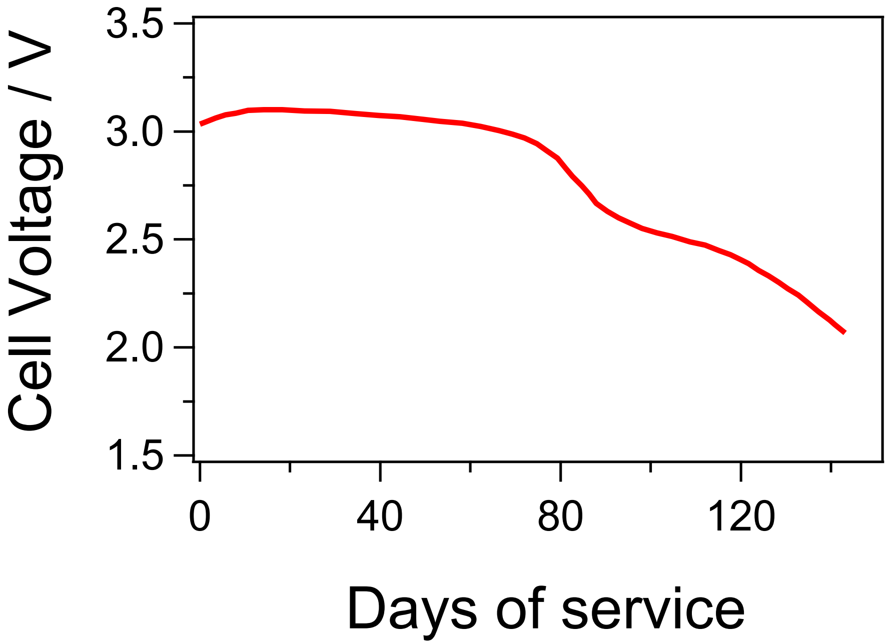
Oxosalts



Exploded view of rectangular (prismatic) Li-Ag_2CrO_4 pacemaker cell (by courtesy of SAFT Gipelec)

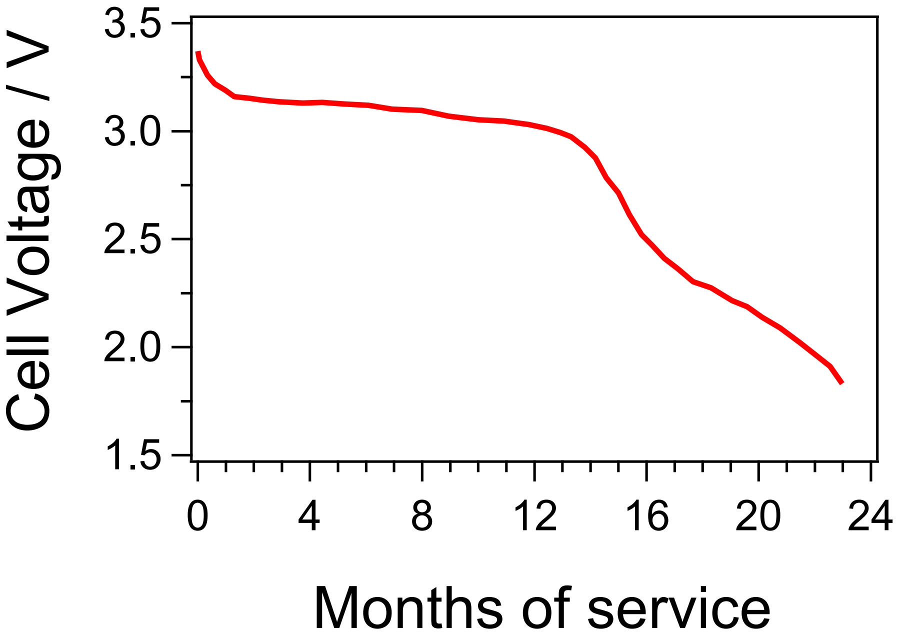
Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM



Accelerated discharge curve for a Li-Ag_2CrO_4 pacemaker cell of nominal capacity 600 mAh (SAFT Gipelec Li210), under a load of 15 kΩ.

Oxosalts



Discharge Characteristic of a Li-Ag_2CrO_4 pacemaker cell of nominal capacity 600 mAh (SAFT Gipelec Li210), under a load of 75 kΩ.

A limited amount of swelling occurs during discharge, due to the positive volume change associated with the cell reaction. With some salts, such as Ag_2PO_4, this problem is more severe.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Oxides**

The discharge reaction for Li-MeO cells is almost always more complex than the formal displacement process:

$$2Li_{(s)} + MO_{(s)} \rightarrow Li_2O_{(s)} + M_{(s)}$$

For example:

- ✓ Bi_2O_3 and PbO give rise to intermetallic compounds such as Li_3Bi and LiPb;
- ✓ MoO_3 and V_2O_5 form ternary phase.

In many cases (e.g. for the MnO_2 cathode) the discharge mechanisms are still not fully understood.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Oxides**

Theoretical capacities for a number of simple displacement reactions involving oxides

Active cathode material	Product	Electrons involved	Capacity $Ah{\cdot}kg^{-1}$	$Ah{\cdot}dm^{-3}$
Bi_2O_3	Bi	6	0.350	3.070
CuO	Cu	2	0.670	4.260
MnO_2	Mn_2O_3	1	0.310	1.550
Pb_3O_4	Pb	8	0.310	2.850

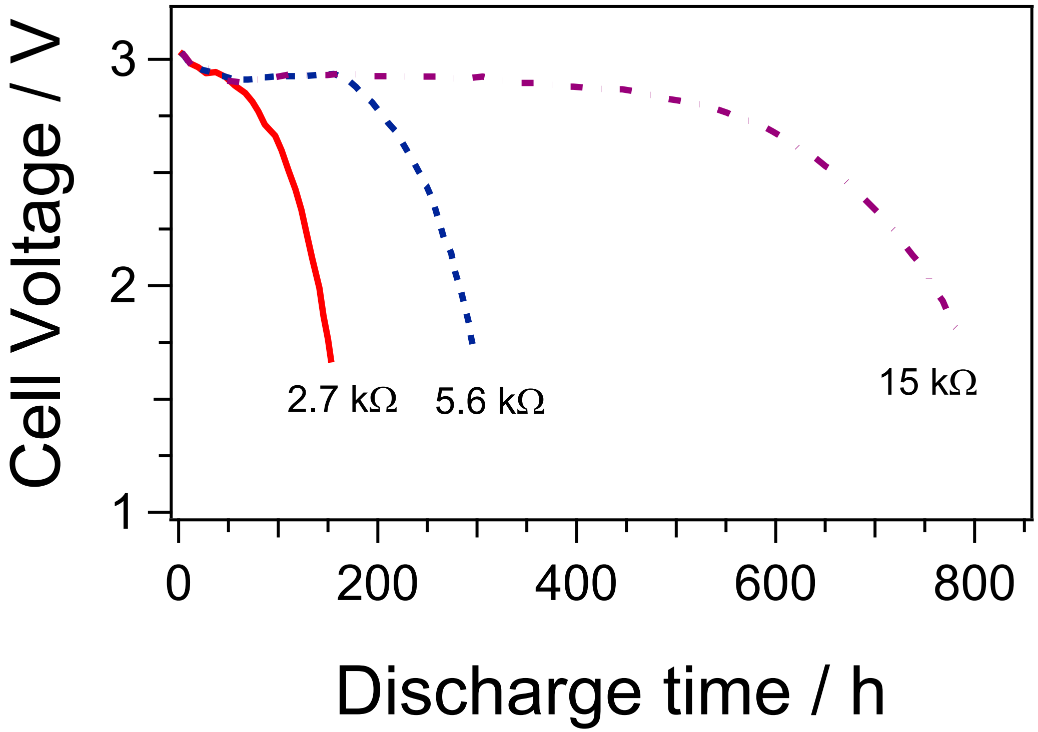
Two categories of cell may be distinguished:

‘**high voltage**’ and ‘**voltage compatible**’.

The latter term refers to the fact that lithium cells with discharge voltages of about 1.5 V can readily replace the more conventional miniature aqueous cells for which much electrical equipment has been designed.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Oxides**

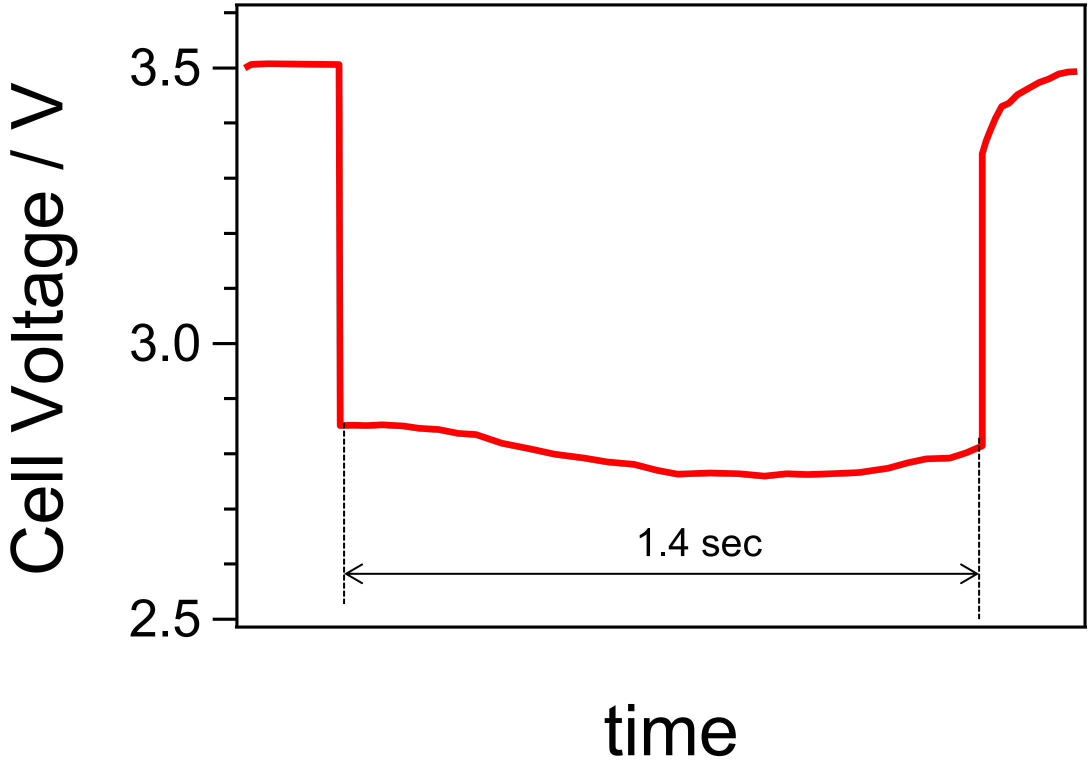


Discharge curves of Li-MnO$_2$ button cells (Varta CR2025) under various loads at T$_{amb}$

The Li-MnO$_2$ high voltage cell introduced by Sanyo in 1975 is now manufactured by numerous companies, using specially prepared high density MnO$_2$. The OCV is in the range 3.0-3.5 V and typical discharge curve are shown on the figure.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Oxides**



Response to high current discharge pulse of a typical Li-MnO_2 watch battery (LM 2020). Current: 6 mA (by courtesy of SAFT Gipelec)

The discharge characteristics and low self-discharge make this a very suitable system for powering electric watches with LCD displays. An important requirement for such a battery is the ability to provide current pulse to illuminate a miniature tungsten bulb (to enable the time to be read at night) while maintaining an acceptable voltage.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Oxides**

The Li-CuO cell is voltage compatible (OCV $\approx$ 1.5 V) and has he highest specific energy of all solid cathode Lithium-based cells. Practical values for complete cells of 750 Wh·dm^{-3} (300 Wh·kg^{-1}) are comparable with those of the Li-SO_2 system. The discharge curve shows a single step which may be attributed to the simple displacement reaction:

$$2Li_{(s)} + CuO_{(s)} \rightarrow Li_2O_{(s)} + Cu_{(s)}$$

It has recently been shown that cathode utilization and shelf-life are improved by incorporation of about 1 m/o of Li_2CO_3 or LiOH in the CuO, followed by heat treatment ('m/o' is used to represent the molar percentage of a component in a mixture).

The electrolyte used varies from manufacturer to manufacturer:

$LiClO_4$ in dioxolane has proved to be a very satisfactory system.

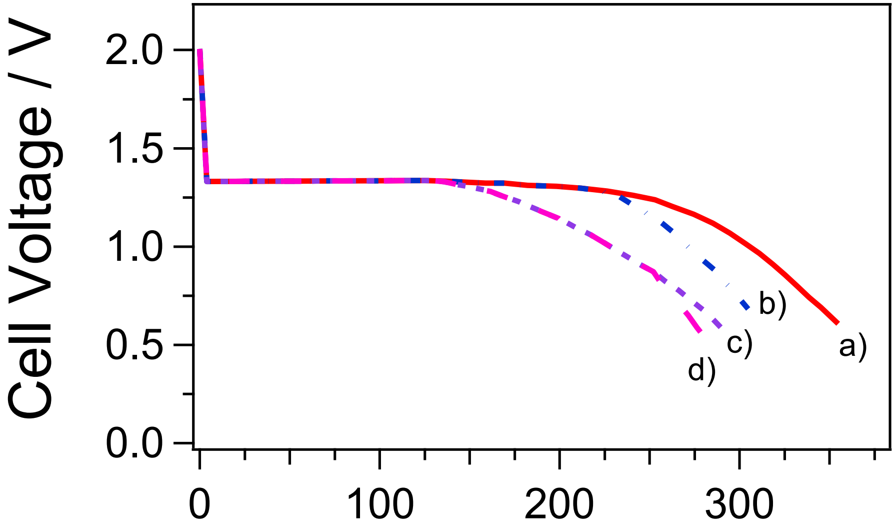
Once again, self discharge is very low.

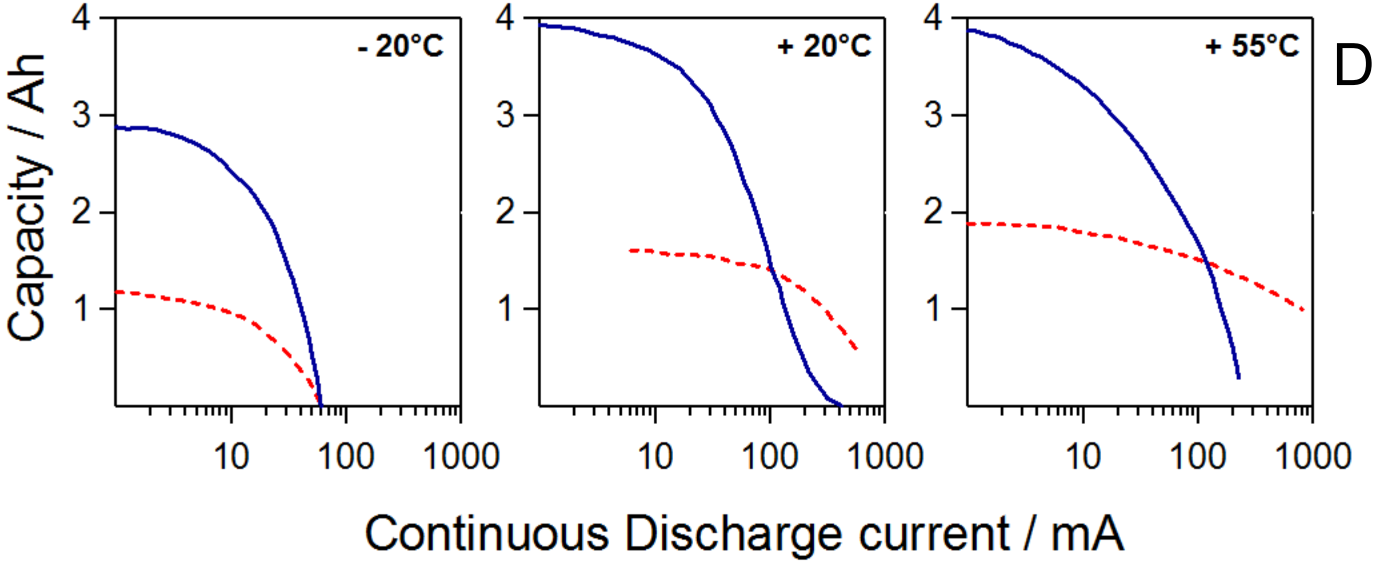
Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM

Oxides

Discharge curves of Li-CuO button cells (LC 01) after accelerated shelf testing at 70°C. a) fresh cell, b) after 6 months at 70°C, c) after 12 months at 70°C, d) after 18 months at 70°C. (by courtesy of SAFT Gipelec)



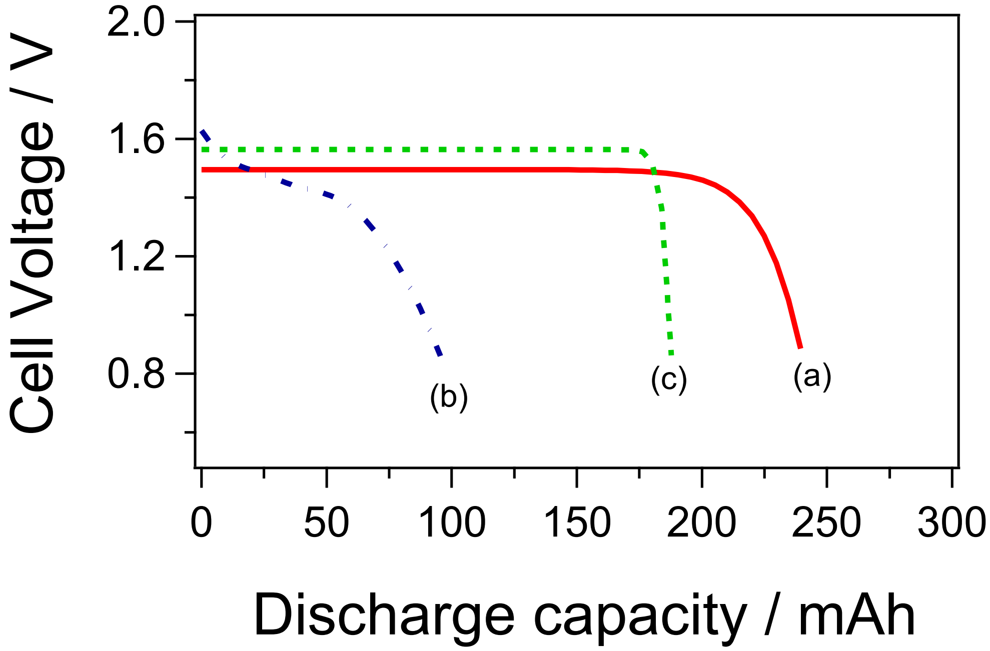


Capacity of Li-CuO button cells (LC 01) as a function of discharge current (solid lines). Dashed lines indicate the characteristics of alkaline manganese cells of similar dimensions. (by courtesy of SAFT Gipelec)

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Oxides**

The cells are manufactures in cylindrical form with theoretical capacities in the range 500 – 3900 mAh. A comparison of practical discharge capacities of Li-CuO button cells and a number of aqueous alternatives is given in picture.



Comparison of discharge curves at ambient temperature of voltage compatible Li-CuO button cells and conventional aqueous cells:

a) Litium-copper oxide

b) Alkaline manganese

c) Zinc-silver oxide

Load: 75 kΩ

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM **Sulphides**

Metal sulphides have the advantage over the corresponding oxides that most of them are good electronic conductors and hence sulphide-based cathodes are not usually require the addition of carbon.

Batteries based on cupric sulphide cells (three in series) have been developed and used with cardiac pacemakers since 1976. reduction of CuS takes place in two stages:

$$2CuS_{(s)} + 2Li_{(s)} \rightarrow Cu_2S_{(s)} + Li_2S_{(s)}$$

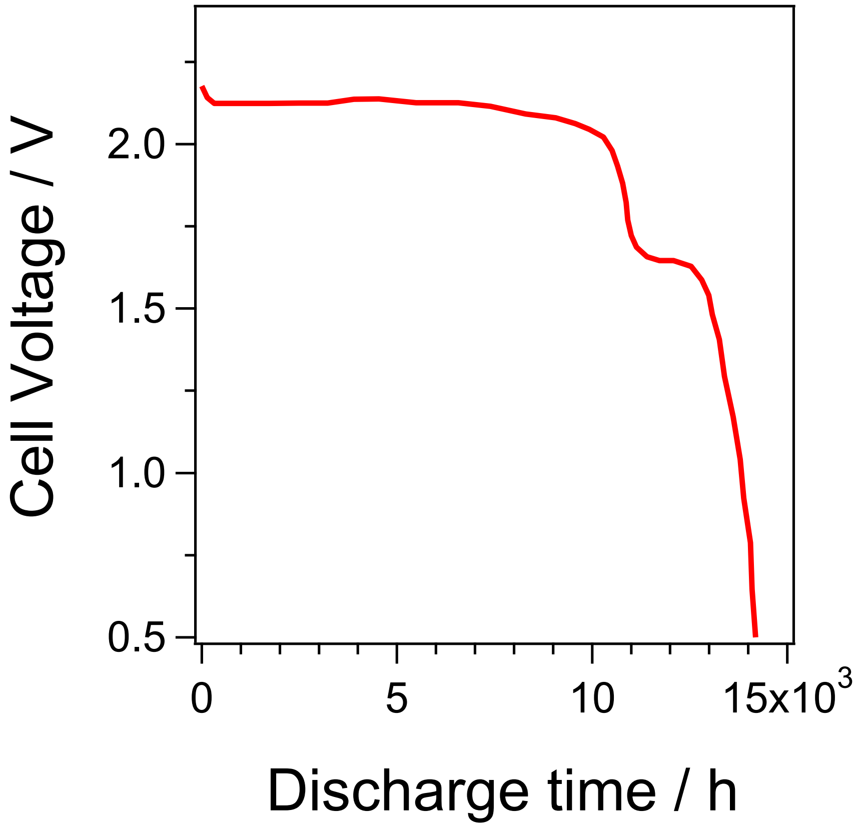
and

$$Cu_2S_{(s)} + 2Li_{(s)} \rightarrow Cu_{(s)} + Li_2S_{(s)}$$

so that the discharge curve has two stages with plateaus at 2.12 V and 1.75V.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM



Discharge curve of a Li-Cupric sulphide pacemaker cell at 37°C under a load of 12.3 kΩ (by permission of the Electrochemical Society)

Sulphides

The Cordis pacemaker cells are anode limited so that about 80% of the cell capacity has been delivered when the fall in cell voltage occurs.

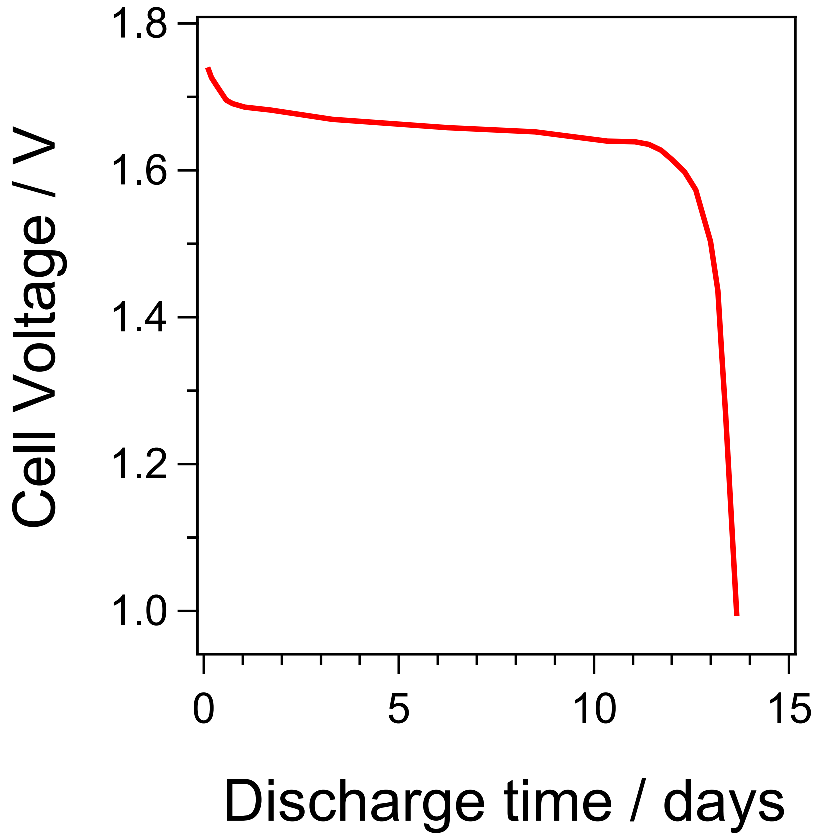
The electrolyte in this cells is $LiClO_4$ dissolved in a mixed solvent, of which the major constituent is dioxolane.

Self-discharge is negligible.

An increase in volumetric capacity of 80% in comparison with aqueous mercury batteries is claimed together with an associate reduction in pacemaker weight.

Ambient lithium liquid electrolyte cells

SOLID CATHODE SYSTEM



Discharge curve of a Li-Cuprous sulphide thin coin cell under a load of 12.5 kΩ (by courtesy of INCO)

Sulphides

Cells based on cuprous sulphide have also been developed: the continuous discharge characteristics of a Ray-O-Vac thin coin cell are shown in picture.

Other promising systems include cells based on iron sulphide cathodes. The best performance has been produced with non-stoichiometric FeS_x, with $x \approx 1.1$.

Ambient lithium liquid electrolyte cells

SOLUBLE CATHODE SYSTEMS

All the currently available commercial lithium cells using a soluble cathodic reagent are based on SO_2.

These advanced cells which have outstanding performances, but also certain drawbacks, have until recently been limited to military uses.

Now they are finding increasing service for heavy duty applications in a wider consumer market.

The cell may be represented as:

$$Li_{(s)}SO_{2,(s)}, LiBr, ANC_{(s)}$$

with an overall reaction:

$$2Li_{(s)} + 2SO_{2,(dis\,s.)} \rightarrow Li_2S_2O_{4,(s)}$$

An OCV of just over 3.0V is observed.

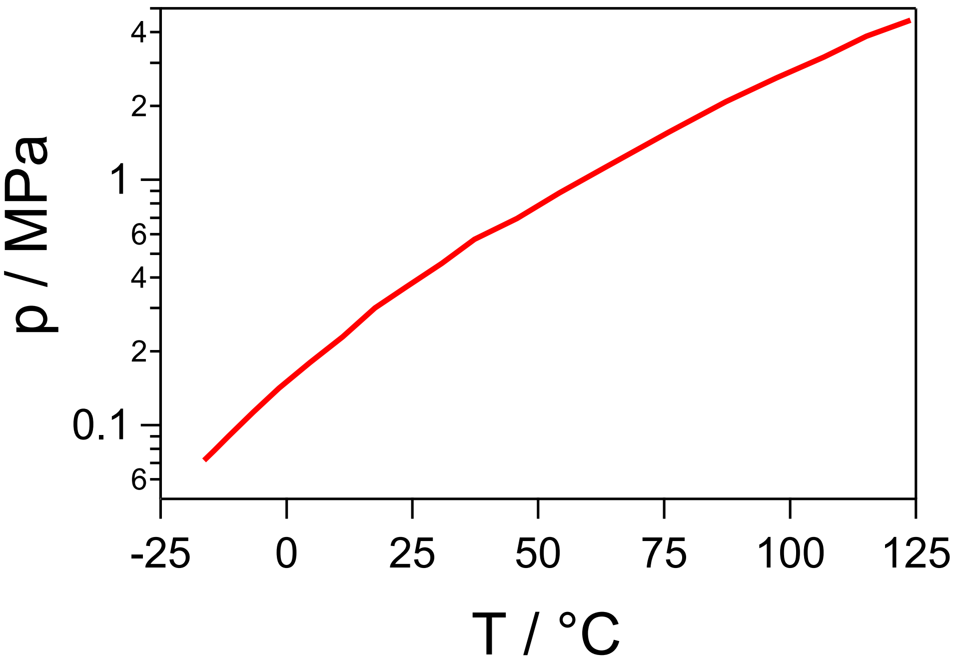
Ambient lithium liquid electrolyte cells

SOLUBLE CATHODE SYSTEMS

A typical electrolyte is a solution of LiBr in AN which has a conductance of 5S·m^{-1} at room temperature, failing to 2S·m^{-1} at -50°C.

This rather small reduction leads to excellent low temperature discharge characteristics.

The concentration of dissolved SO_2 in an undischarged cell at room temperature gives rise to an internal pressure of about 300 kPa (3 atm).



Internal pressure of Li-SO_2 cells as function of Temperature (by permission of Elsevier Sequoia S.A.)

The internal pressure decrease as the cell is discharged. However the pressure increases to 3 MPa (30 atm) at 100°C. , so that the engineering problems associated with designing and fabricating a safe container and seals are severe.

Ambient lithium liquid electrolyte cells

SOLUBLE CATHODE SYSTEMS

Non è possibile visualizzare l'immagine.

Li-SO2 spiral cell. (by permission of Elsevier Sequoia S.A.)

The cells have a spiral wound construction as illustrated schematically in Figure.

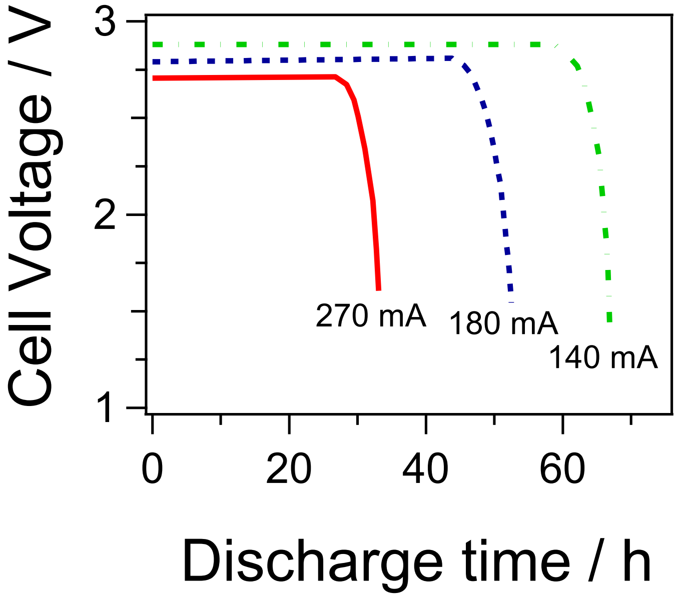
The lithium foil strip is separated from the cathodic current collector, a carbon black/teflon mix, by a thin microporous propylene separator. A Nickel plated steel case encloses the spiral and acts as the negative terminal. The positive connector is attached to the cathode via a central tantalum post enclosed in a glass-to-metal seal. The can is hermetically sealed and the liquid phase is injected through a filling eyelet or ‘fillipoint’ which is then welded shut. A safety vent is located at the bottom of the cell to prevent rupture of the outer case if the internal pressure were to rise above the safety limit

Ambient lithium liquid electrolyte cells

SOLUBLE CATHODE SYSTEMS

Li-SO_2 cells are characterized by energy densities of up to 330 Wh·kg^{-1} (525 Wh·dm^{-3}) which are four times as high as the best zinc cell value. because of the low internal resistance of the spiral wound cells, the discharge voltage of 2.8 – 2.9 V is hardly affected by the rate of discharge.

It can be seen that the discharge profiles are flat, with negligible voltage delay.



Discharge curves for D-size Li-SO_2 cells at ambient temperature as function of current. (by permission of Elsevier Sequoia S.A.)

At present, Li-SO2 cells are manufactured in cylindrical form with capacities ranging from 0.45 to 30 Ah. They are classified as standard or high rate systems. The former are constructed to operate over a wide scale of load and temperature conditions.

Ambient lithium liquid electrolyte cells

SOLUBLE CATHODE SYSTEMS

The latter are designed to deliver a high energy output at low operating temperatures.

Applications in the military area take advantage of the high power density and unrestrictive operating conditions, and include providing power for portable radio transceivers, night vision equipment, sonobuoys, missiles and ‘artillery delivered’ device.

Emergency systems, alarms, aircraft emergency locators, etc…, are typical examples of civilian uses.

Li-SO2 cells are characterized by high energy density, high power density, good voltage regulation, exceptional low temperature performance and superior shelf-life.

Ambient lithium liquid electrolyte cells

SOLUBLE CATHODE SYSTEMS

The real problem is that if the cells are abused they may explode or vent a highly toxic gas. Exposure of the cell to high temperatures, either external or internally generated by prolonged short circuit conditions, may raise the internal pressure to dangerous levels.

Further, after storage at 60°C for extended periods, some corrosion of the glass-to-metal seal has been observed. As usage changes from predominantly military to civilian applications, even more stringent safety standards become essential.

In particular, improvements in seal and vent technology must be made. A separate problem which must be solved before the use of this system becomes widespread, concerns the safe disposal of spent cells.

Ambient lithium liquid electrolyte cells

LIQUID CATHODES

A number of inorganic molecules such as thionyl chloride ($SOCl_2$), sulphuryl chloride (SO_2Cl_2) and phosphoryl chloride ($POCl_3$) have been found capable of acting both as solvent and as cathodic reagent in lithium cells. Such materials are liquid over a wide temperature range, and can dissolve considerable quantities of salts such as $LiAlCl_4$ to give conductive solutions.

They show excellent kinetic stability towards lithium, due to the formation of passivating layers. Liquid cathode electrode cells have many similarities to the Li-SO_2 system, except that no organic component is present.

Ambient lithium liquid electrolyte cells

LIQUID CATHODES

Properties of liquid cathode materials

	Phosphoryl Chloride	**Sulphuric Chloride**	**Thionyl Chloride**
Formula	$POCl_3$	SO_2Cl_2	$SOCl_2$
Relative MM	153.33	134.97	118.97
m.p. / °C	2	-54.1	-105
b.p. / °C	105	69.1	78.8
ε_r	13.3 (22°C)	10 (22°C)	9.25 (20°C)
μ / N·m^{-2} x 1000	0.921 (25°C)	0.674 (25°C)	0.603 (25°C)
ρ / g·cm^{-3}	1.67 (25°C)	1.6 (25°C)	1.65 (25°C)

It is seen that thionyl chloride has the widest liquid range: commercial interest has been focused mainly on this system

Ambient lithium liquid electrolyte cells

LIQUID CATHODES

The Li-$SOCl_2$ cell may be represented as:

$$Li_{(s)}\left|LiAlCl_4, SOCl_{2,(l)}\right|C_{(s)}$$

with the main cell reaction

$$4Li_{(s)} + SOCl_{2,(l)} \rightarrow 4LiCl_{(s)} + SO_{2,(diss.)} + S_{(s)}$$

The OCV is approximately 3.6 V. The generally accepted mechanism involves the initial formation of SO at the carbon cathode current collector. This molecule dimerises and finally decomposes to form sulphur and sulphur dioxide:

$$SOCl_2 + 2e^- \rightarrow SO + 2Cl^-$$
$$2SO \rightarrow (SO)_2$$
$$(SO)_2 \rightarrow S + SO_2$$

Ambient lithium liquid electrolyte cells

LIQUID CATHODES

The cell reaction thus leads to the formation of relatively insoluble lithium chloride at the cathode which under some circumstances may block the porous carbon current collector, leading to an increased internal resistance.

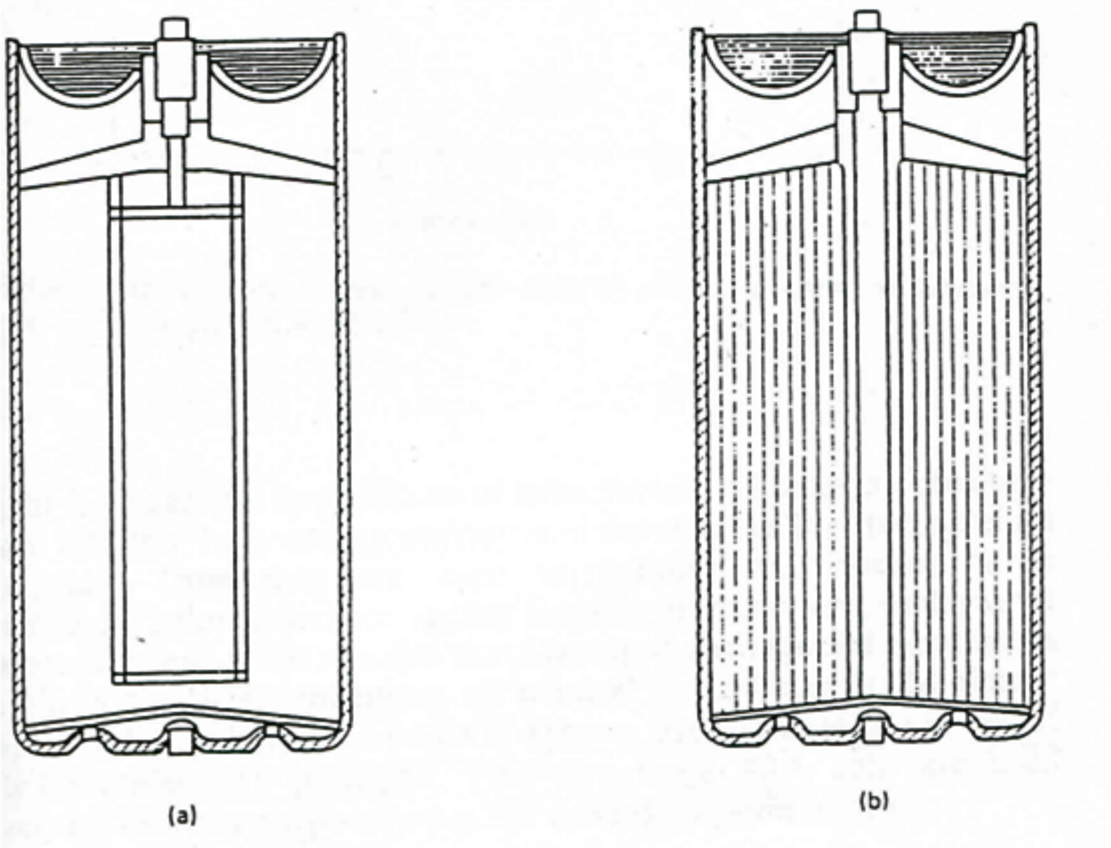
Another product is SO_2, which may lead to an increasing internal pressure as the discharge continues. However in practice most of the SO_2 remains dissolved and the pressure build up is small.

Further electrochemical reduction of SO_2 to form lithium dithionite may also occur.

A number of other possible reactions have been suggested, and as utilization of $SOCl_2$ is much higher at low current drains, it would appear that the overall reaction is a function of the discharge rate.

Ambient lithium liquid electrolyte cells

LIQUID CATHODES



Schematic structure of D-size lithium-thionyl chloride cells:
a) high energy type, b) high power type

Practical cells are mainly of the cylindrical or button type. The former may be designed with slightly different internal structures for high energy or high power applications.

Ambient lithium liquid electrolyte cells

LIQUID CATHODES

The high energy cell is a bobbin-type unit, while the high power cell has a spiral construction giving a large electrode area.

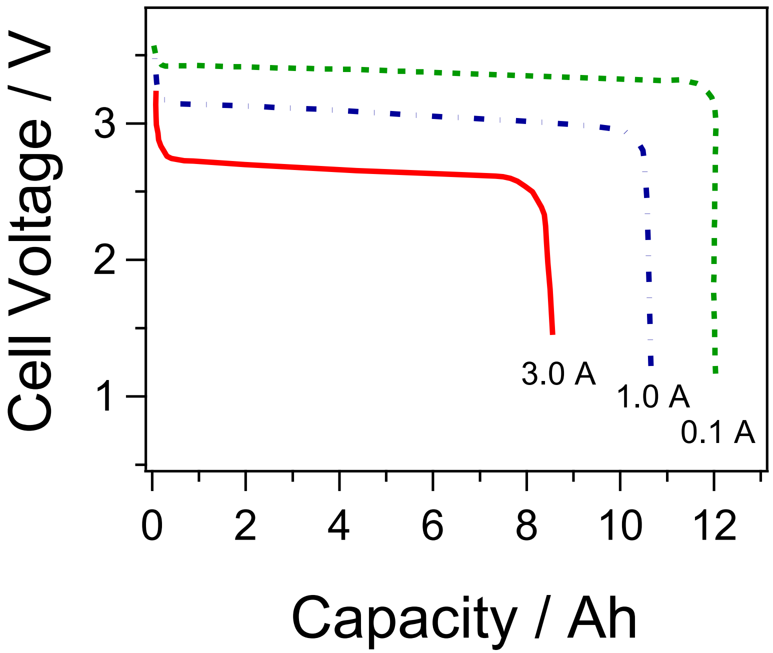
The cathode current collector is again a porous carbon black/Teflon mix. Since $SOCl_2$ is a very aggressive chemical, there are special problems of material compatibility in cell fabrication. The cell case is constructed of nickel or nickel plated stainless steel and must ne hermetically sealed to a helium leakage rate of 10^{-9} $cm^3 \cdot s^{-1}$ or better.

Normal plastics and rubbers are unstable in thionyl chloride and only fully fluorinated polyolefins such as Teflon can be used as insulators. Early manufacturing problems concerned with attack on glass-to-metal seals have been solved.

Much larger cells with capacities up to 10 000 Ah and 40 A discharge capabilities have recently been tested, and a 1.2 MWh 30 V battery has been developed for military use.

Ambient lithium liquid electrolyte cells

LIQUID CATHODES



Discharge curves of D-size Lithium-thionyl chloride cells at ambient temperature

At room temperature, discharge curves are exceptionally flat even at rates of up to 3A for D-sized cells. As noted above, SOCl2 utilization is much higher at low current drains. Low rate cells manufactured by Mallory with a spiral configuration (4.45 cm x 25-38 cm electrodes) produced practical energy densities of 661 Wh·kg^{-1} (1240 Wh·dm^{-3}) at 0.01 A. At temperature of -30°C and below (the working range for such cells is generally quoted as -40°C to +75°C), some advantage delay is evident at higher current densities.

Ambient lithium liquid electrolyte cells

LIQUID CATHODES

Reasonably flat discharge curves are still developed for currents of 0.1 A and below (for D-sized cells), while 3A can still be drawn without undue polarization, although the cell capacity is much reduced. Shelf-life is excellent, with an estimated capacity loss of less than 0.5% per annum over a three year period.

Many of practical applications of lithium-thionyl chloride ells take advantage of their high energy density and favorable low temperature characteristics. Thus they are used in balloon and rocket borne meteorological radiosondes, emergency locating transmitters, underwater instrumentation, etc… Cells are also manufactured with special dimensions and terminals for direct mounting on printed circuit boards. Miniature (button) cells based on the Li-SOCl2 system are used in a variety of implanted biotelemetry packages. The very large 40 A cells are used exclusively for military purposes, i.e. for driving torpedo motors.

Ambient lithium liquid electrolyte cells

LIQUID CATHODES

Sulphuryl chloride, when coupled with lithium, has an even higher density than thionyl chloride. The OCV of the cell

$$Li_{(s)}\left|LiAlCl_4, SO_2Cl_{2,(l)}\right|C_{(s)}$$

is 3.91 V at 30 °C. manufacturing problems with such a cell are very similar to those of the Li-$SOCl_2$ system, so that it is expected that commercial developments of this cell will follow quite rapidly.

Phosphoryl chloride suffers from a relatively high melting point (2 °C) and a consequently restricted liquid range.

Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS

The lithium electrode

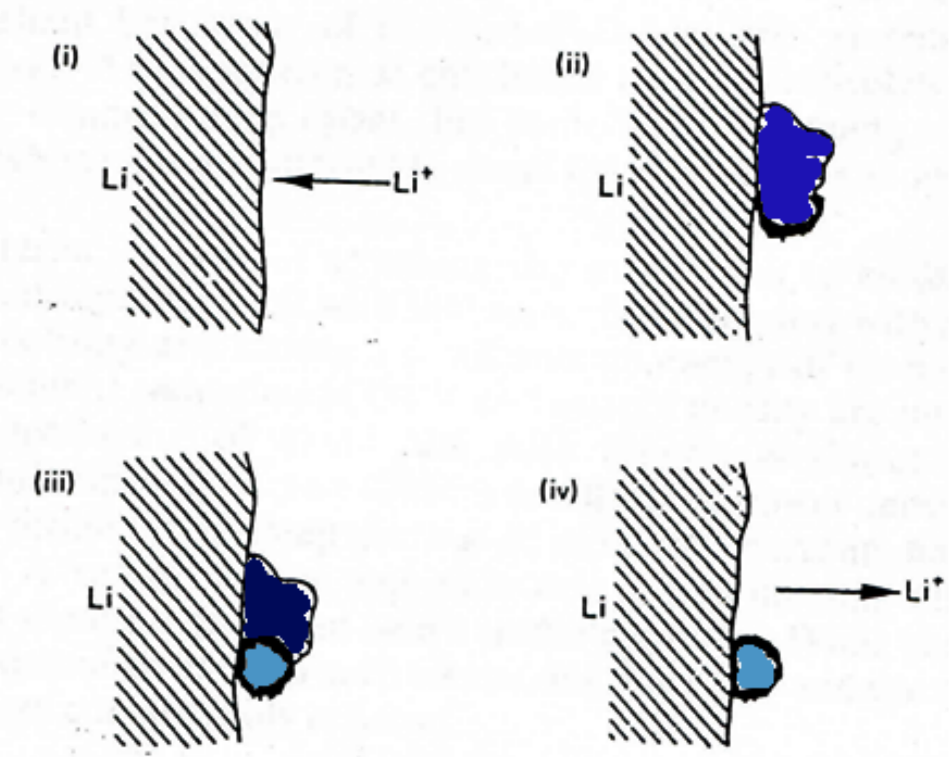
The existence of a passivating film on lithium surfaces in contact with an organic solvent-based electrolyte was discussed earlier.

Film formation ensures long shelf-life for lithium cells, but causes severe problems for good lithium electrode cyclability.

It is found that lithium can be plated with virtually 100% efficiency in a range of organic systems; however the plated lithium cannot be stripped quantitatively, especially if the cell has been allowed to stand for a period between plating and stripping.

Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS



Mechanism for isolation of plated lithium by an insulating film, as suggested by S.B. Brummer of EIC Corporation

The lithium electrode

The Li is considered to be electrodeposited in granular form and the newly created surfaces react rapidly with components of the electrolyte, and this continues once the charging (plating) current has been switched off.

Some lithium grains become partially undercut and others are completely isolated from the underlying lithium metal by an insulating film. Discharge (stripping) efficiency is therefore less than the 100% and the residual isolated lithium grains affect the morphology of any subsequent replating. After few cycles, the capacity or Ah-efficiency of the cycle falls to almost zero.

Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS **The lithium electrode**

It was found that by altering the constituents of the electrolyte the nature of the passivating film could be modified to such an extent that the cycling behavior was greatly improved.

One of the best electrolytes to date contains $LiAsF_6$ dissolved in carefully purified 2-methyltettrahydrofuran (2-Me-THF).

This solvent was selected because of:

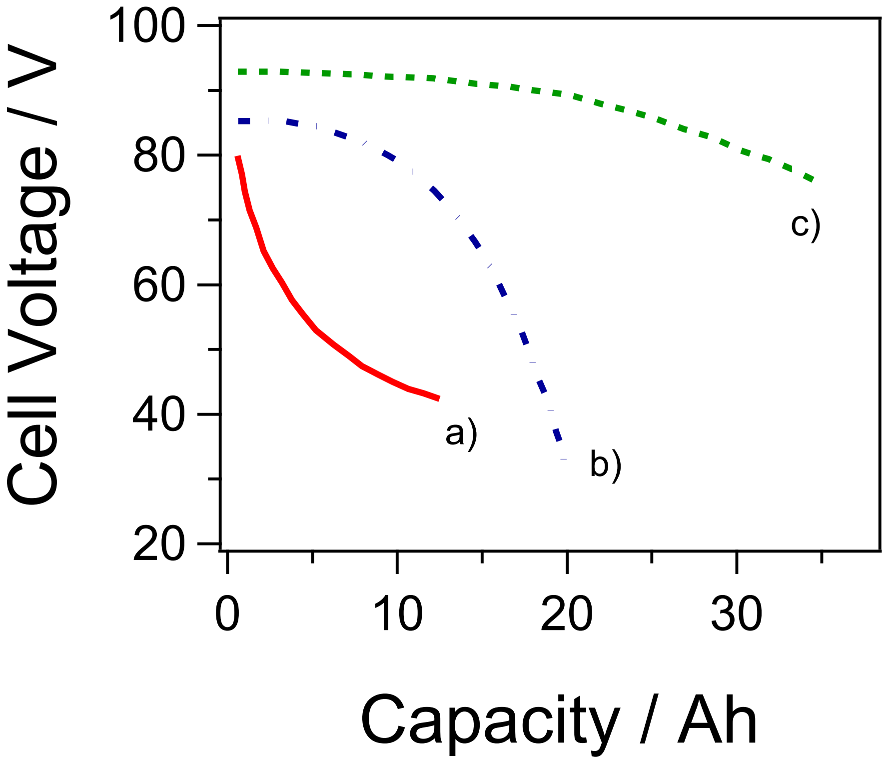
a) the relatively low polarity of the C-O ether bond

b) the predicted effect of the methyl group on slowing the formation of ring-opened products by Li.

The effect of changing the electrolyte constituent is the reason for the excellent behavior of the $LiAsF_6$/2-Me-THF system are not fully understood.

Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS



The lithium electrode

Effect of electrolyte composition on lithium cyclability, after results by V.R. Koch et al. of EIC Corporation:

a) $LiClO_4$, PC-purified electrolyte,

b) $LiAsF_6$, PC,

c) $LiAsF_6$, 2-Me-THF

An experimental cell based on this electrolyte has sustained over one hundred deep cycles, but some loss in stripping efficiency is still evident when cells are allowed to stand for long periods at open circuit.

Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS **The lithium electrode**

An alternative way of attacking the problem is to modify the lithium phase.

Aluminum reacts with lithium to form an alloy with relatively high lithium mobility and having a small enough energy of formation such that the consequent reduction in OCV and energy density are small.

However, alloying/dealloying of aluminum with lithium is slower than the electrodeposition/stripping on pure lithium and thus the power density is reduced.

Further, problems in deep cycling at moderate currents have still to be resolved.

A rather similar approach uses a non-metallic lithium host as anode, of the type discussed below under cathodes. While good cyclability has been demonstrated for such electrodes, the OCV and energy and power densities are considerably reduced.

Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS **Positive electrodes and cells**

Transition metal chalcogenides often form electronically conducting phases that are able to react either chemically or electrochemically with lithium in a reversible manner to form ‘insertion’ or ‘intercalation’ compounds: i.e

$$xLi + TiS_2 \rightleftharpoons Li_xTiS_2$$

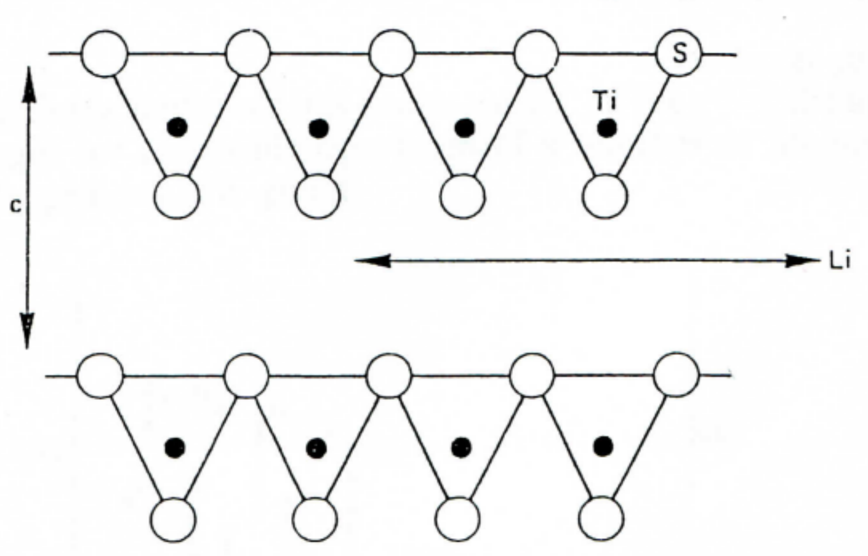
This behavior is related to the structure of the ‘host’ materials: in many cases structure has layers or channels which incorporate guest atoms so that a ternary phase can be formed with a minimum of structural perturbation.

Thus an almost limitless number of charge/discharge cycles are possible without significant degradation of the structural or electrical properties of the host lattice.

Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS

Positive electrodes and cells



The **Ti atoms** are held between hexagonally close-packed **S atoms** to form layer which are held together by weak van der Waals forces. Incorporation of **Li atoms** between the layer produces a continuous and reversible variation of the c-lattice parameter but no phase change.

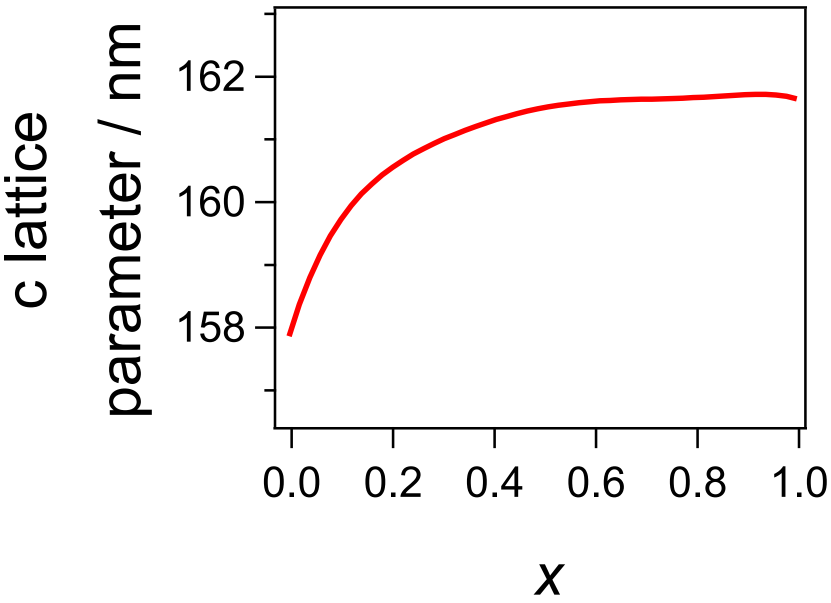
In many cases, the mobility of Li in the host lattice is reasonably good (e.g. the diffusion coefficient of Li in TiS_2 is $2x10^8$ $cm^2{\cdot}s^{-1}$ at room temperature), so that concentration polarization is not unacceptably high.

The electrode potential of Li_xTiS_2 with respect to Li falls from above 2.4 V to 1.9 V as *x* rises from 0 to 1.

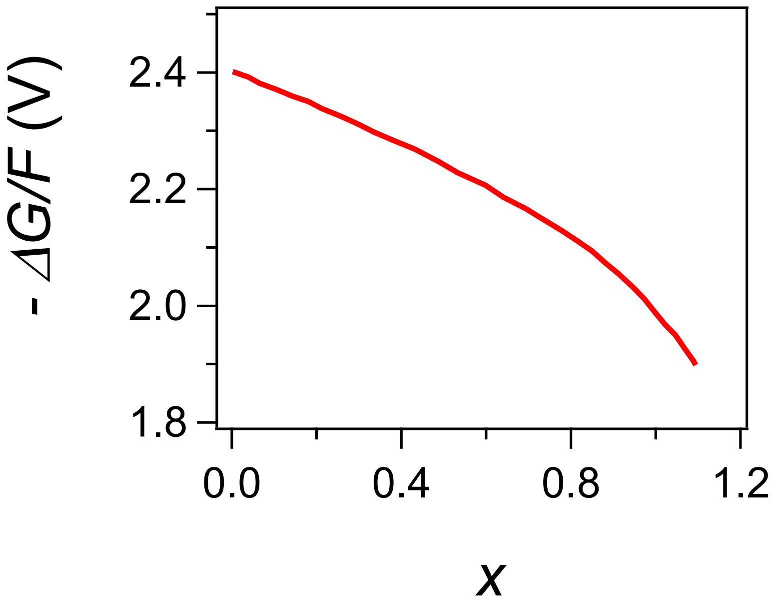
Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS

Positive electrodes and cells



Variations of c-lattice parameter with x in Li_xTiS_2*. (by permission of the Electrochemical Society)*

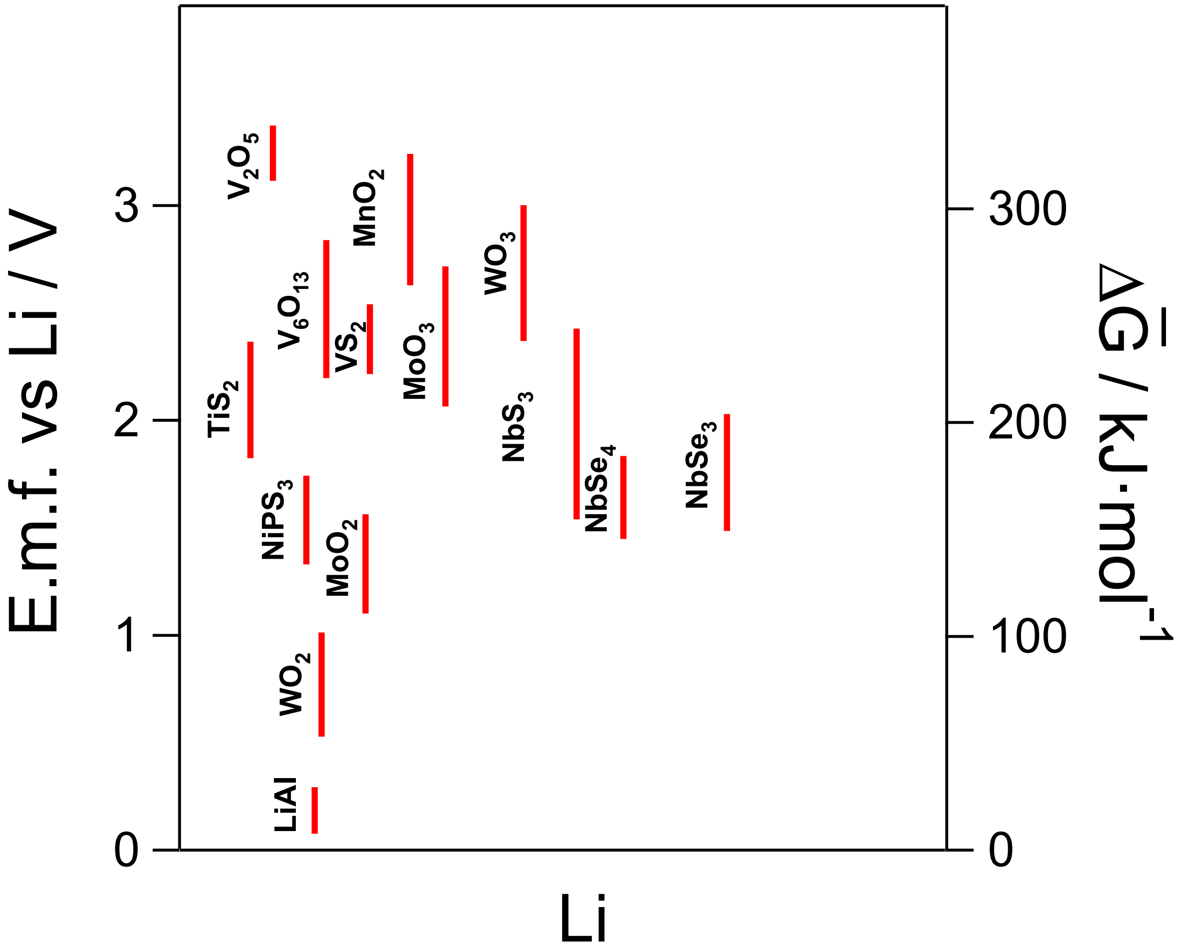


Variations of c-lattice parameter with x in Li_xTiS_2*. (by permission of the Electrochemical Society)*

Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS

Positive electrodes and cells



Voltage ranges for reversible operation of materials which may be coupled with Li, after F.A. Trumbore (by permission of Pure and Applied Chemistry)

A wide range of possible reversible cathode materials has been studied.

Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS

Positive electrodes and cells

	Structure	Reaction	Pot. Range vs Li / V	Theor. En. den. / $Wh\cdot kg^{-1}$	Cyclability
TiS_2	Layered, 2-D	$xLi+TiS_2 = Li_xTiS_2$ $0<x<1$	2.6 – 1.9	480	Prolonged cycling at 80% depth
V_6O_{13}	Rutile, 3-D	$xLi+V_6O_{13}=Li_xV_6O_{13}$ $0<x<7.9$	2.8 – 2.2	800	Prolonged cycling in the $0<x<0.7$ range
$NbSe_3$	Fibrous, 2-D	$xLi+NbSe_3=Li_xNbSe_3$ $0<x<3$	2.2 – 1.2	440	Over 200 deep cycles
Mo_8O_{23}	Framework, 3-D	$xLi+Mo_8O_{23}=Li_xMo_8O_{23}$ $0<x<0.8$	2.8 – 2.0	1000	Prolonged cycling at 40% depth
TiO_2	Anatase, 3-D	$xLi+TiO_2=Li_xTiO_2$ $0.2<x<0.6$	2.0 – 1.0	950	Prolonged cycling in the $0.1<x<0.3$ range

The reactions are of the topochemical type, involving insertion in a host lattice with minimum pertubation in the host structure

Ambient lithium liquid electrolyte cells

SECONDARY SYSTEMS **Positive electrodes and cells**

It should be noted that the Li (anode) cyclability problem has limited the commercial development of such cells to the single example of the LiAl-TiS_2 cell.

This miniature cell was manufactured by Exxon in two sizes with capacities of 25 mAh and 90 mAh. It had a nominal voltage range of 1.5 – 2.1 V and was rated for a minimum of five cycles at 1 mA to 80% of nominal capacity. Due to limited commercial success, production was discontinued.

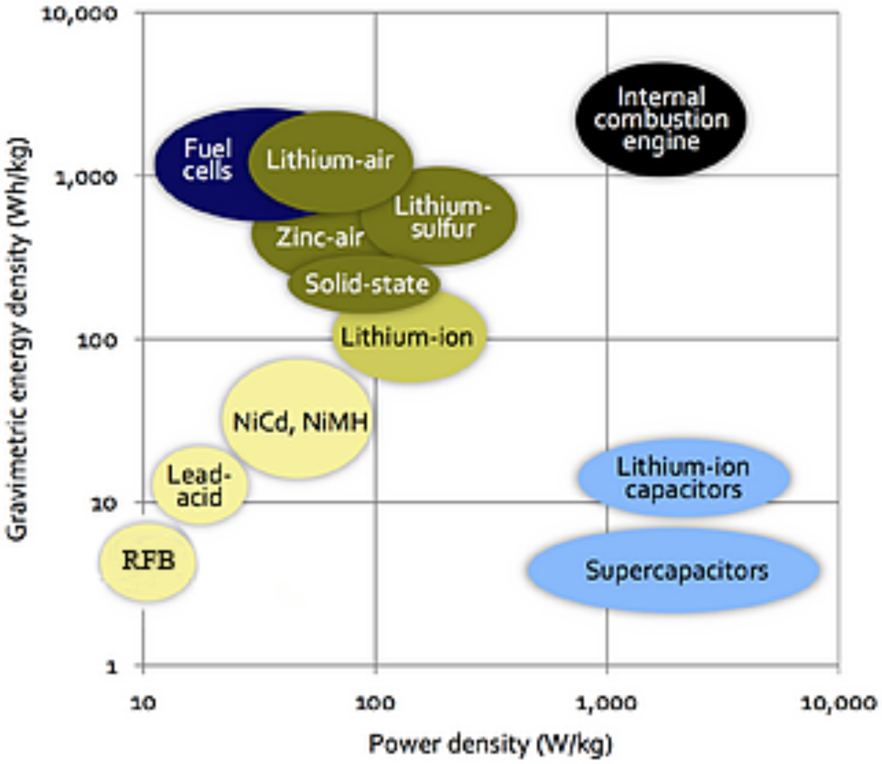
The original intention was to develop EV and load leveling batteries based on this system. However after considerable research it was found that the technical problems were too severe to proceed further at this time.

Lithium-ion or “Roching-chair” batteries

Lithium-inserting solid-state anodes are used in place of lithium and the lithium ions shuttle between interstitial sites in the intercalating cathode and anode.

The advantages of such batteries lie in:

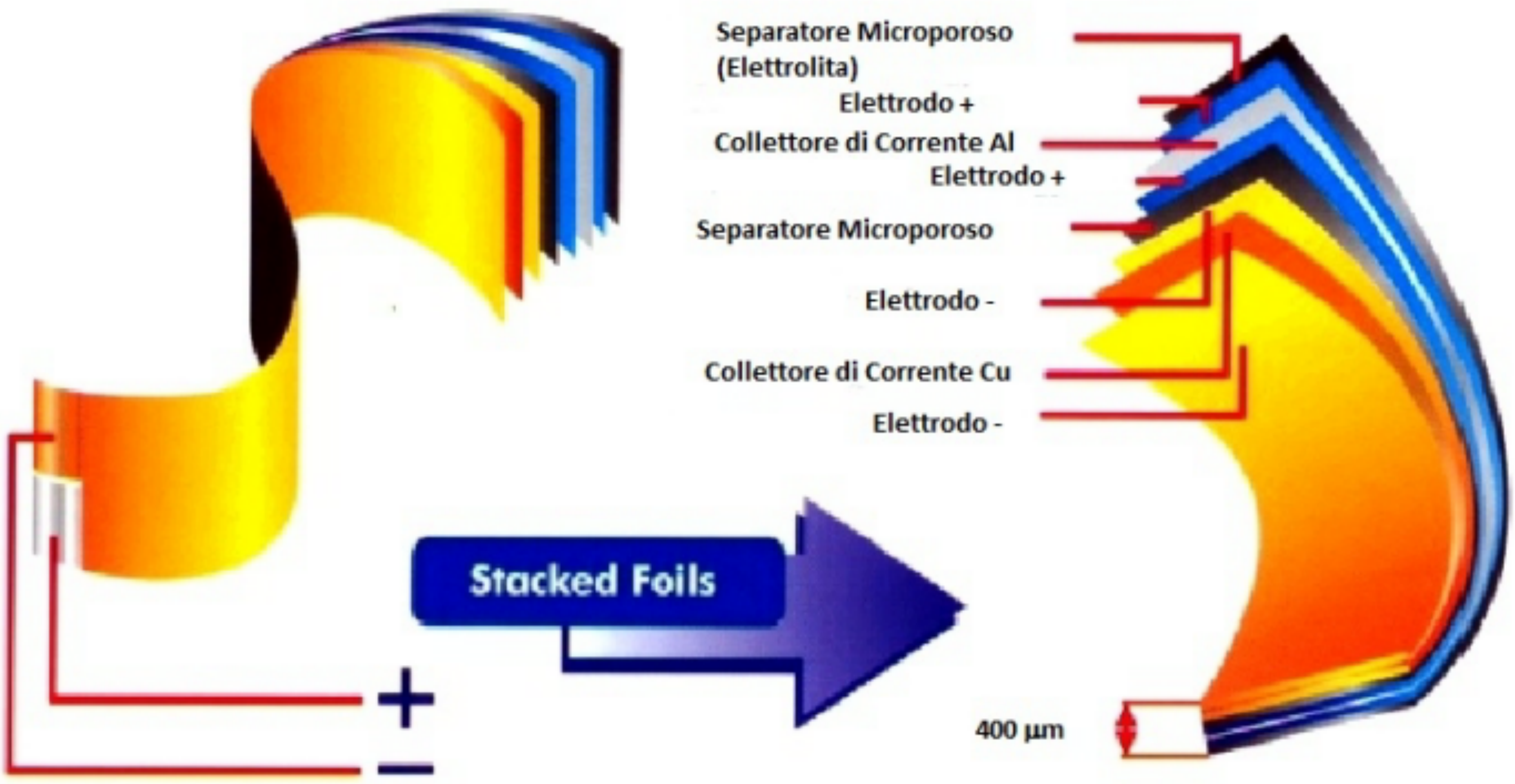
- ✓ Their superior safety over cells containing Li metal;
- ✓ The high anode cycling efficiency as the anodic reactions do not involve plating and stripping of metallic Li;
- ✓ Fast anode reaction kinetics as there should be no passivating layer to plate through



Lithium-ion or “Roching-chair” batteries

SECONDARY SYSTEMS

Positive electrodes and cells



Rechargeable Li-ion battery: arrangement of the film electrodes

Lithium-ion or "Roching-chair" batteries

As s anode, the carbon host should fulfill at least three points:

- ✓ High capacity
- ✓ Excellent reversibility
- ✓ High current density of lithiation

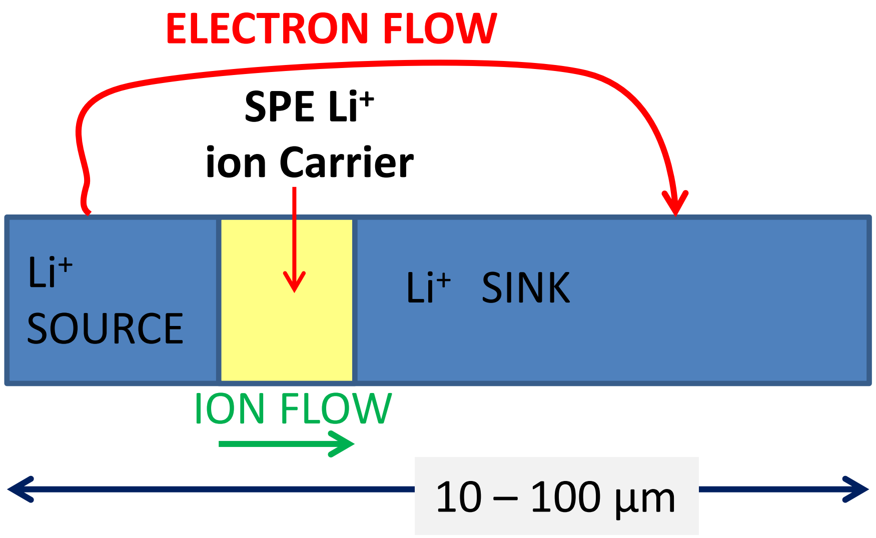
Graphitic and pyrolytic carbons have been found to be the most promising, in forms such as graphite, high-temperature-treated petroleum cokes and high-temperature-treated **mesophase carbon microbeads** (**MCMB**).

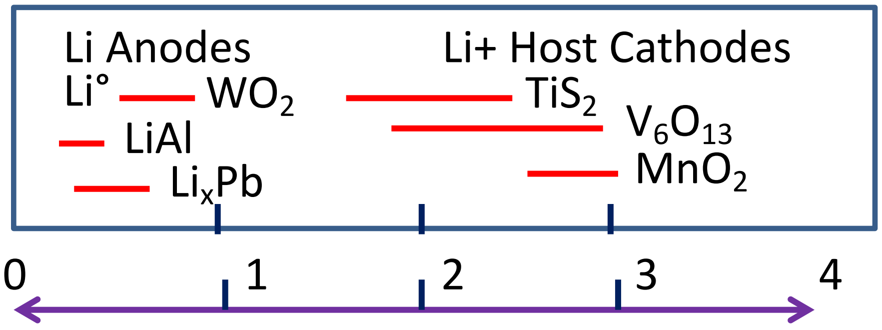
Theoretical capacity of various anode materials by weight and by volume

Anode material	Useful range of x	Capacity / $mAhg^{-1}$	Capacity / $mAhcm^{-3}$
$(1-x)$Li (metal)	1	3861	2062
$(1-x)$Li (metal)[a]	0.25	965	515
Li_xC_6 (coke)	0.5	186	372
Li_xC_6 (graphite)	1	372	837

[a] ***practical Li metal anode that includes a fourfold excess of Li for sufficient cycle life***

Lithium-ion or “Roching-chair” batteries





The lithium-ion batteries that are presently at an advanced developmental stage are generally based on an organic liquid electrolyte with bulk ionic conductivities of the order of 10^{-2} to 10^{-3} Scm^{-1}. it is not surprising, therefore, that the development of polymer electrolyte batteries based on lithium-ion technology was followed on from this. A number of companies are known to be developing lithium-ion based polymer electrolyte batteries but there is limited disclosure of results in the literature

Lithium-ion or “Roching-chair” batteries

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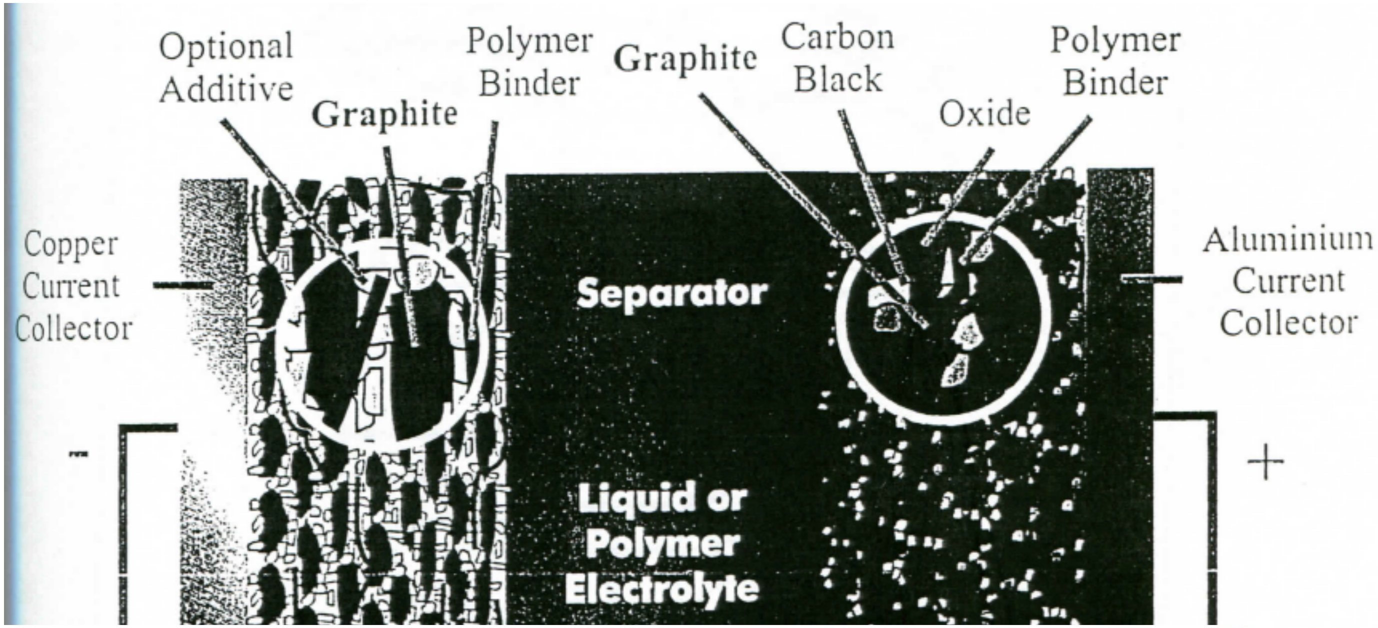
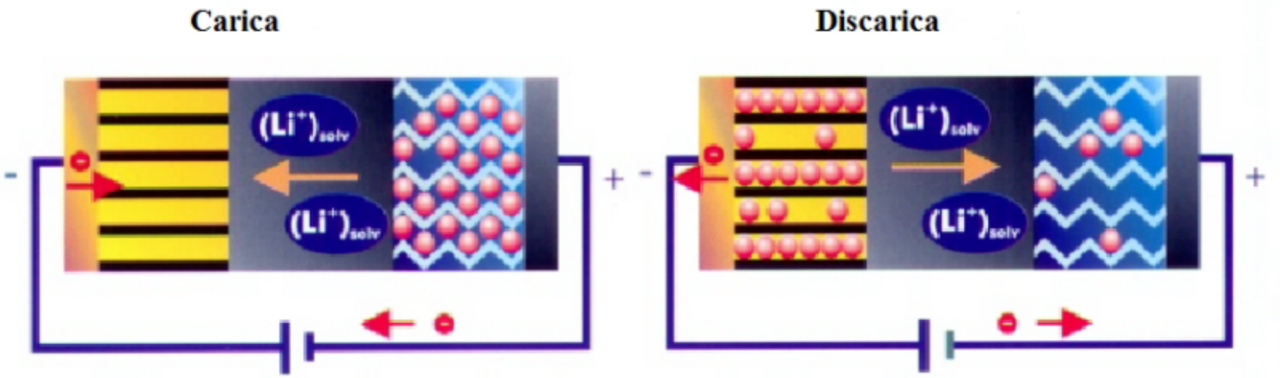
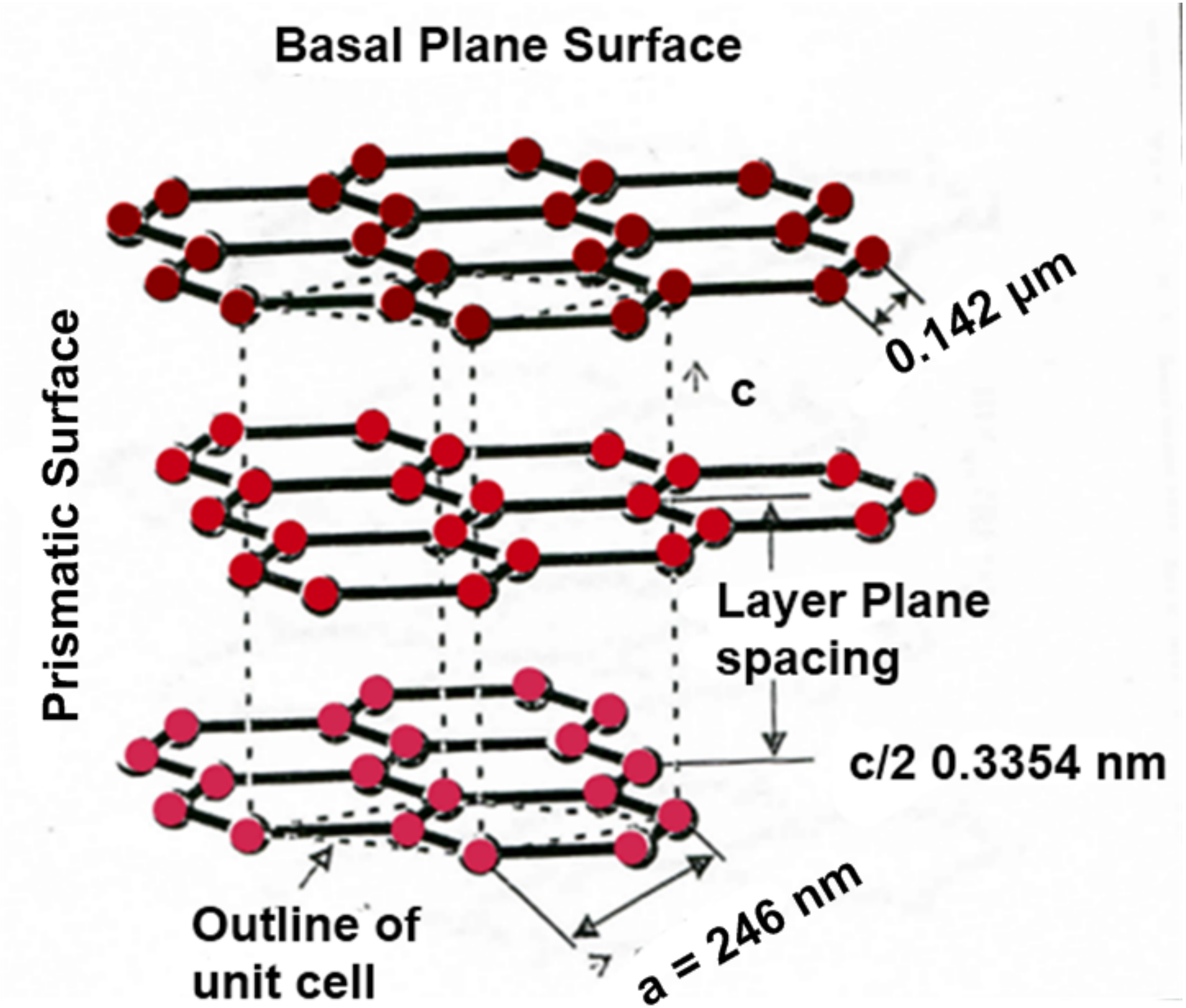




$LiMeO \rightarrow Li_{1-x}MeO + x\ e^- + xLi^+$
$C_6 + x\ Li^+ + x\ e^- \rightarrow Li_xC_6$

$Li_{1-x}MeO + x\ e^- + xLi^+ \rightarrow LiMeO$
$Li_xC_6 \rightarrow C_6 + x\ Li^+ + x\ e^-$

Lithium-ion or “Roching-chair” batteries



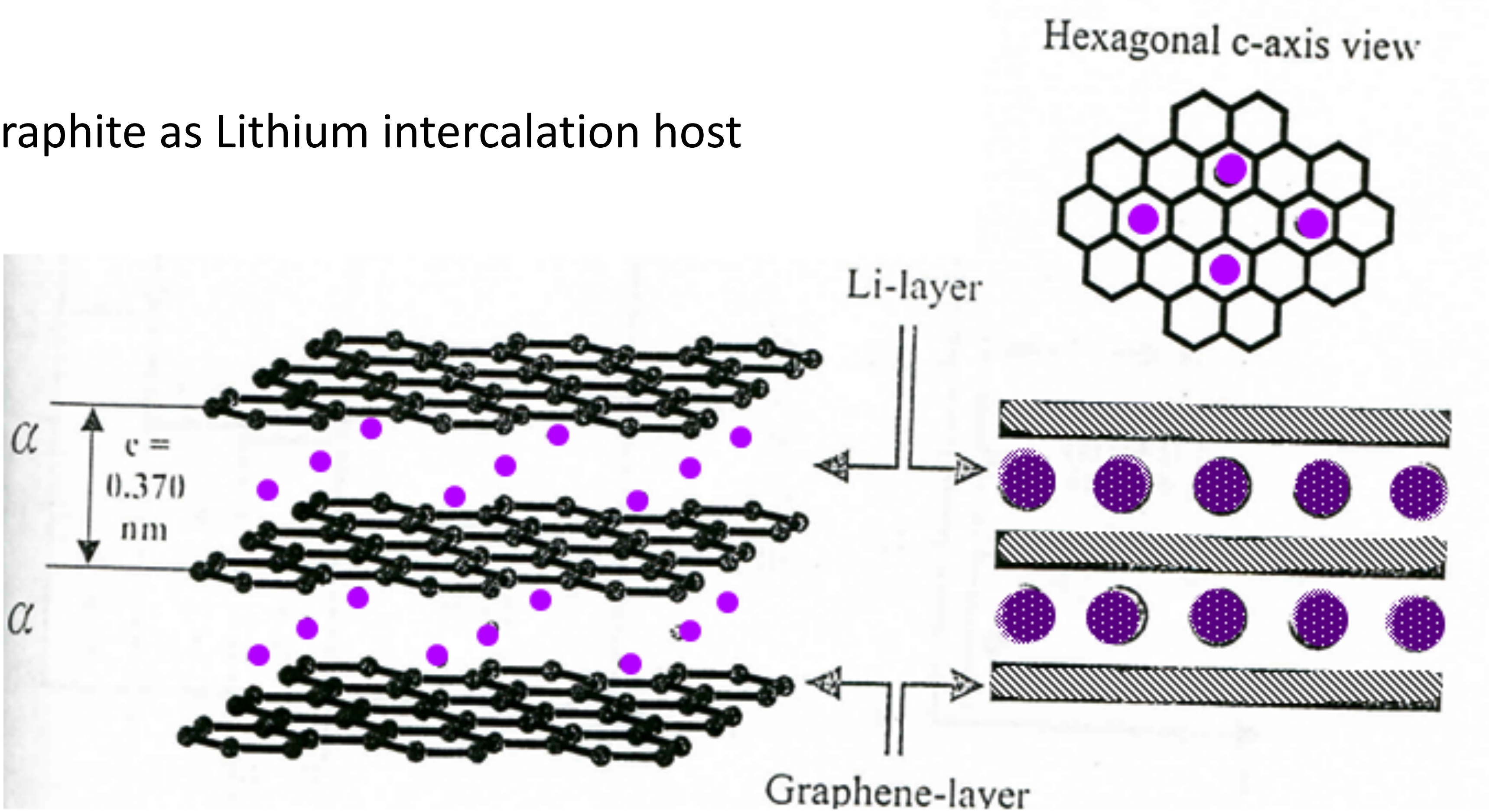
Hexagonal crystal structure of graphite

Lithium-ion or “Roching-chair” batteries

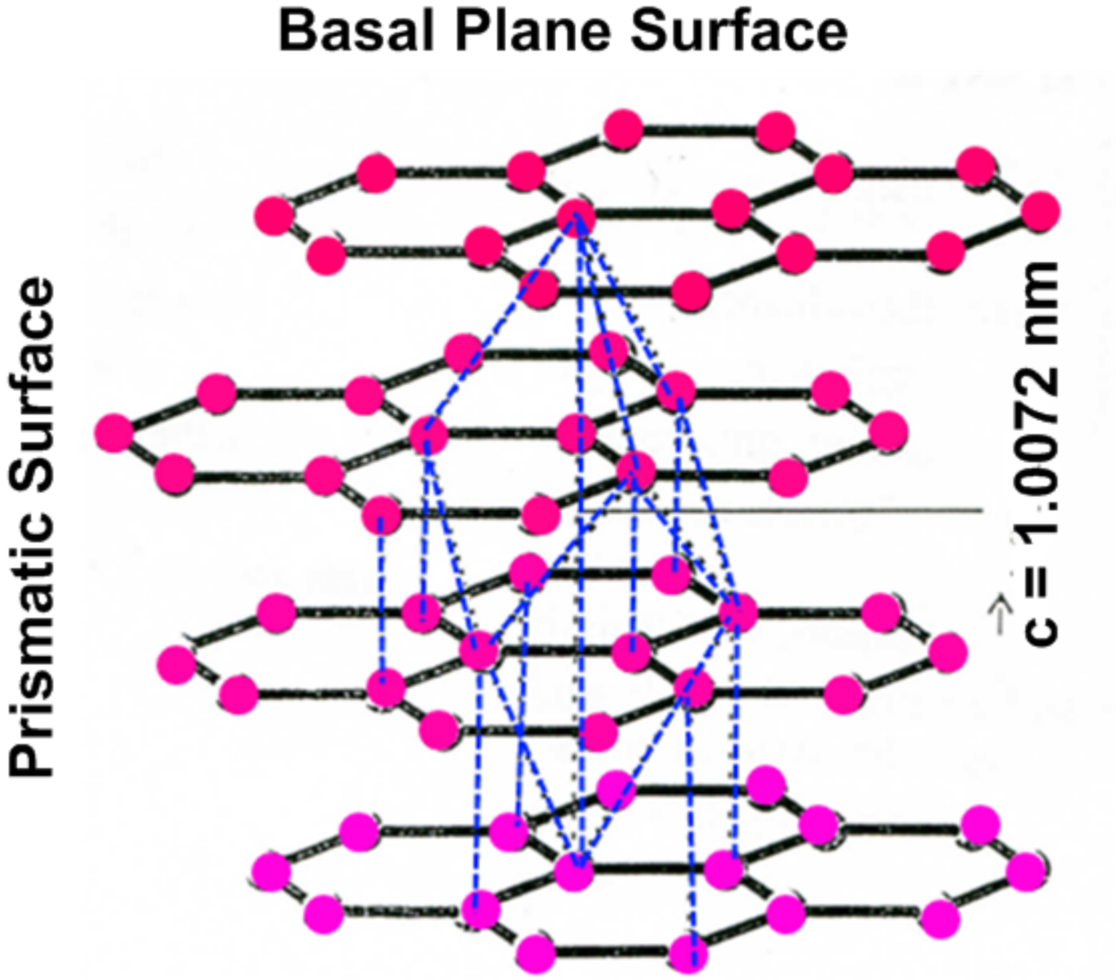
Crystal Structure of LiC6:

- ✓ Electrochemical formation of Li-graphite intercalation compounds;
- ✓ Theoretically obtainable specific charge for LiC6: 372 Ah/kg.

Graphite as Lithium intercalation host

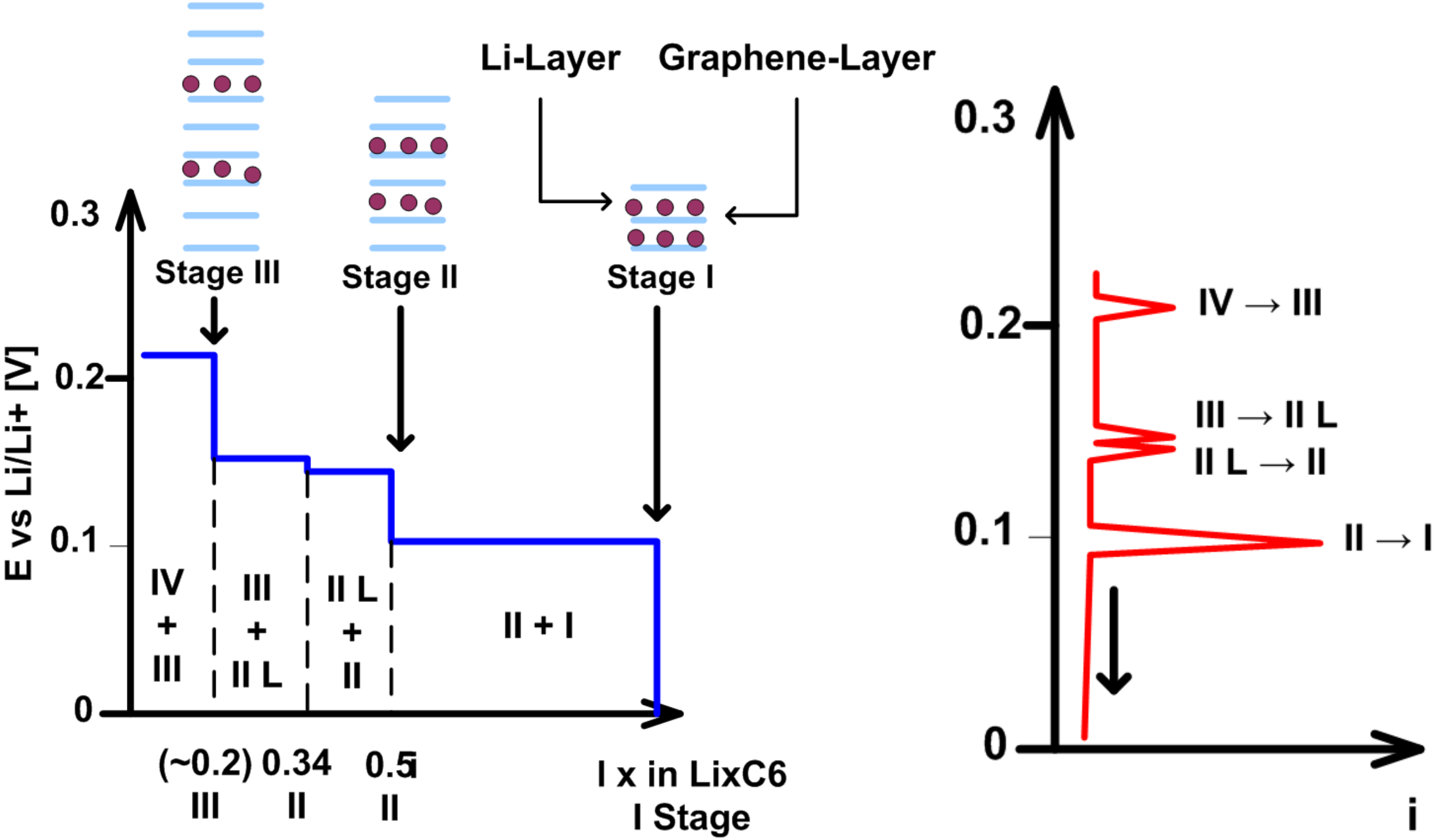


Lithium-ion or "Roching-chair" batteries



Rhombohedral crystal structure of graphite

Lithium-ion or “Roching-chair” batteries



Electrochemical potential as function of the Li content of the graphite electro during the electrochemical Li-intercalation: formation of different Li GIC’s

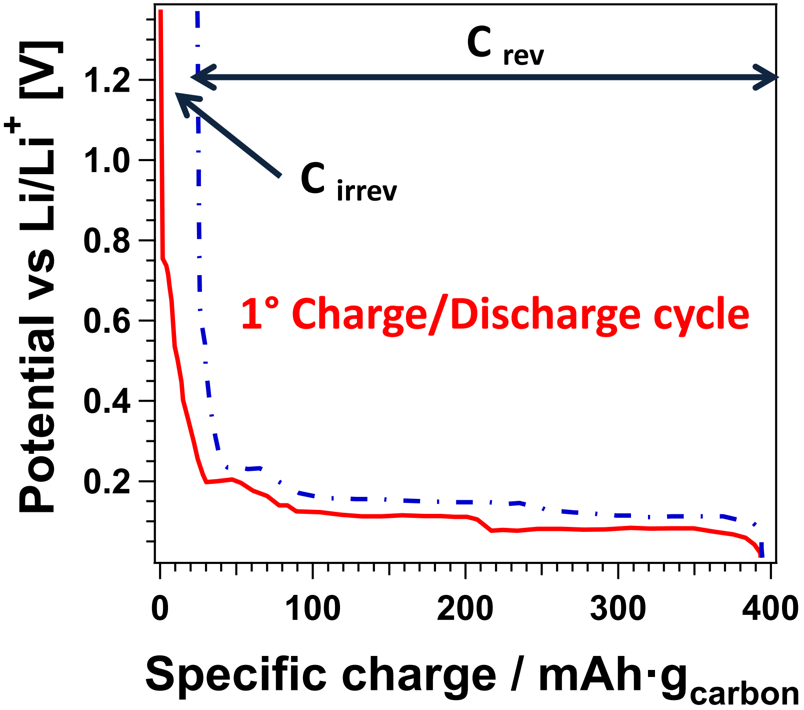
Lithium-ion or “Roching-chair” batteries

Material parameters	Performance in the battery
High crystallinity	High reversible specific charge
High xylene density	High electrical conductivity
High apparent density	High rate capability
High tab density	High cycling stability
High compressibility	Optimized electrode porosities
Ideal pore structure	High energy densities
Optimized BET surface area	Low charge losses in the first electrochemical reduction
	Reasonable price/performance ratio

Lithium-ion or “Roching-chair” batteries

Irreversible capacity in the 1st intercalation cycle

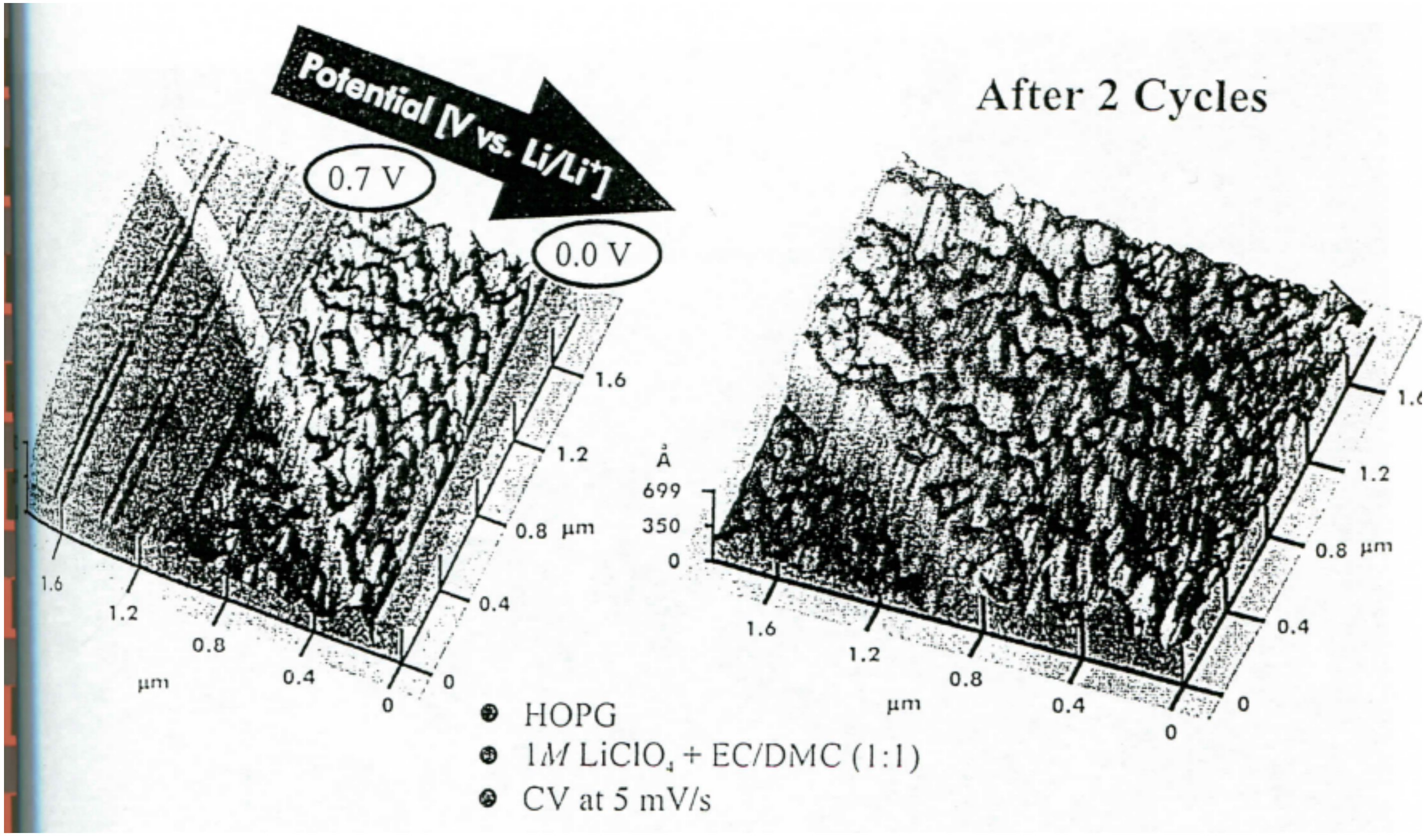
Although causing a charge loss in the cell, the formation of a passivation layer on the graphite particles is essential for the further charge/discharge process



First electrochemical intercalation and deintercalation of Li in a TIMREX$^{(R)}$ SLX50 electrode in a 1 M LiPF6, EC:DCM (1:1) electrolyte. The irreversible capacity is 6.5%

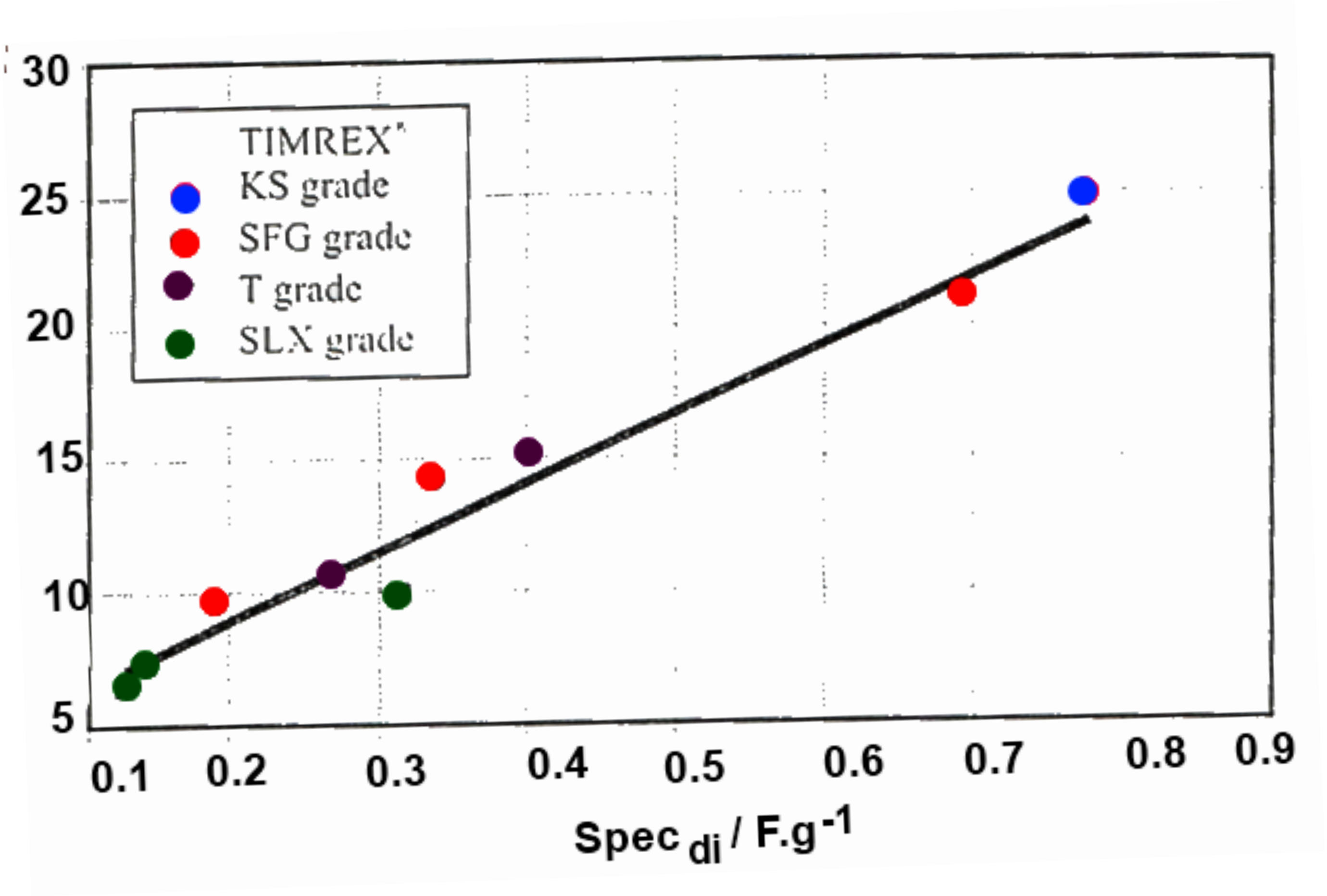
Irreversible capacity in the 1st intercalation of Li+ in a negative graphite electrode: formation of the SEI-layer on the graphite particles (SEI = solid electrolyte interface

Lithium-ion or “Roching-chair” batteries



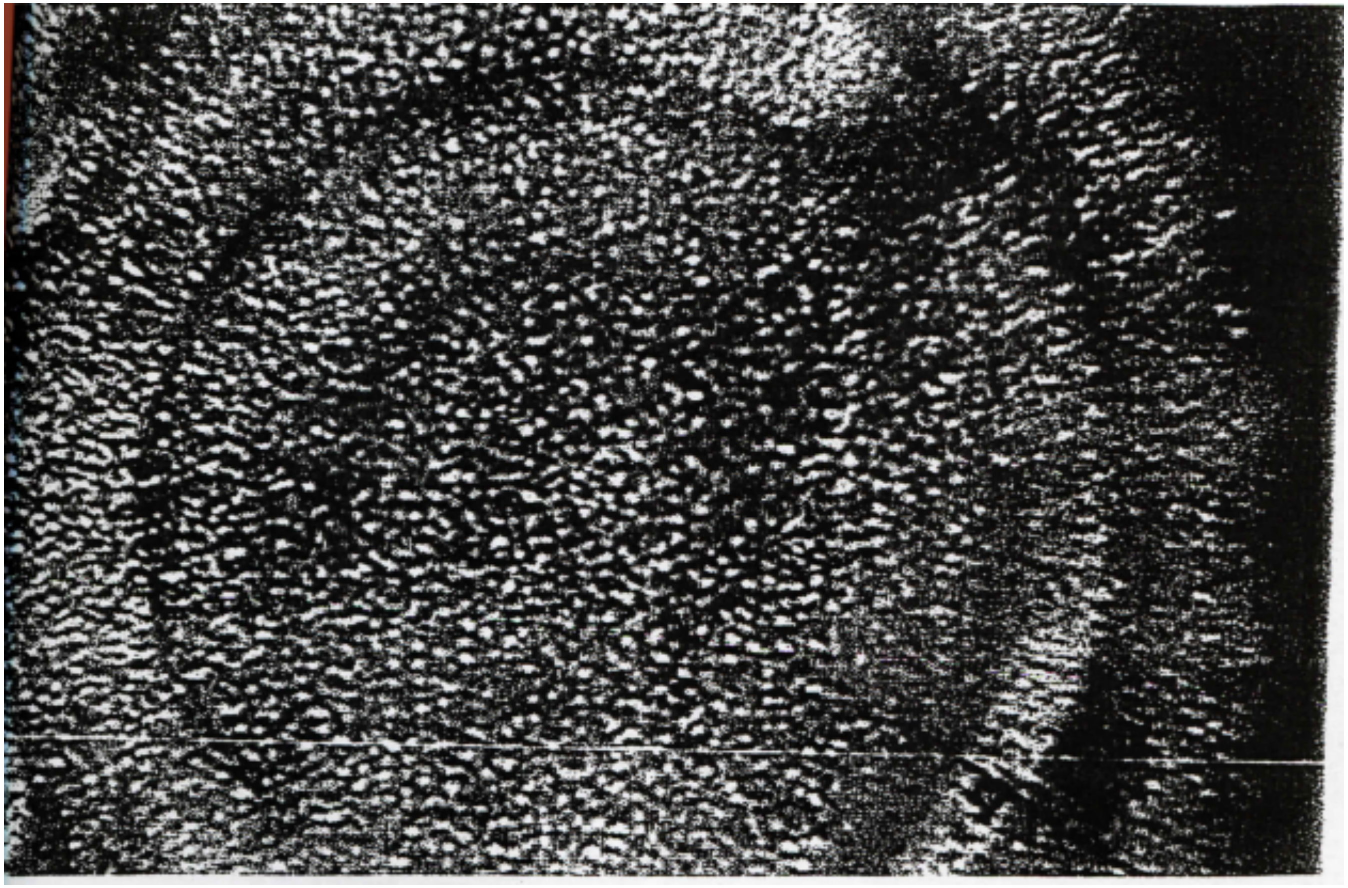
In situ AFM pictures of a highly oriented pyrolytic graphite (HOPG) electrode showing the formation of SEI layer at the HOPG surface at potentials below 0.7 V vs Li/Li$^+$ during the 1st electrochemical insertion (courtesy of PSI)

Lithium-ion or “Roching-chair” batteries



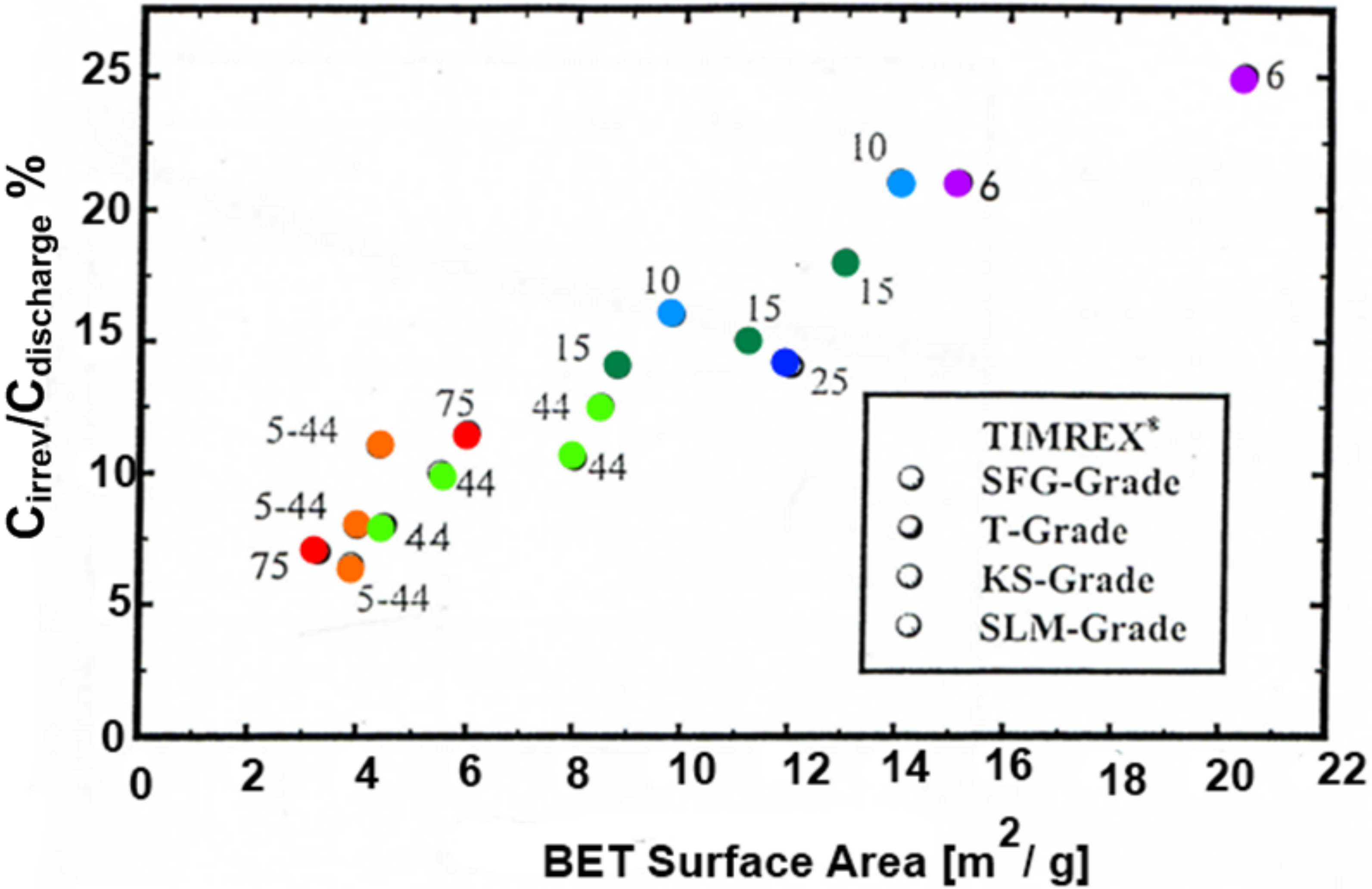
Irreversible capacity of TIMREX$^{(R)}$ standard graphite as a function of the double layer capacitance

Lithium-ion or “Roching-chair” batteries



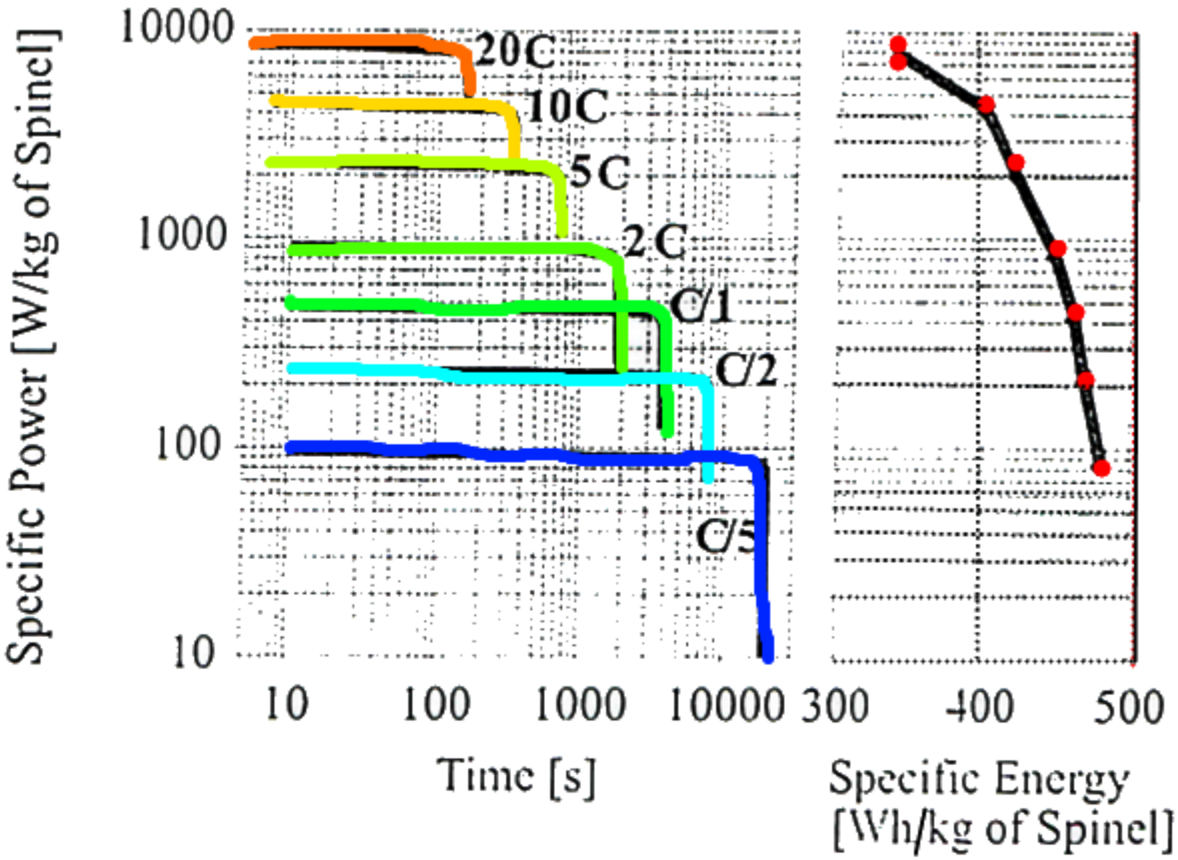
Picture of an in-situ formed graphite negative electrode with a chemical composition of LiC6 (courtesy of PSI)

Lithium-ion or "Roching-chair" batteries



Difference of the BET surface area of the graphite negative electrode material on the irreversible capacity during the 1st charge/discharge cycle of the lithium-ion cell

Lithium-ion or "Roching-chair" batteries

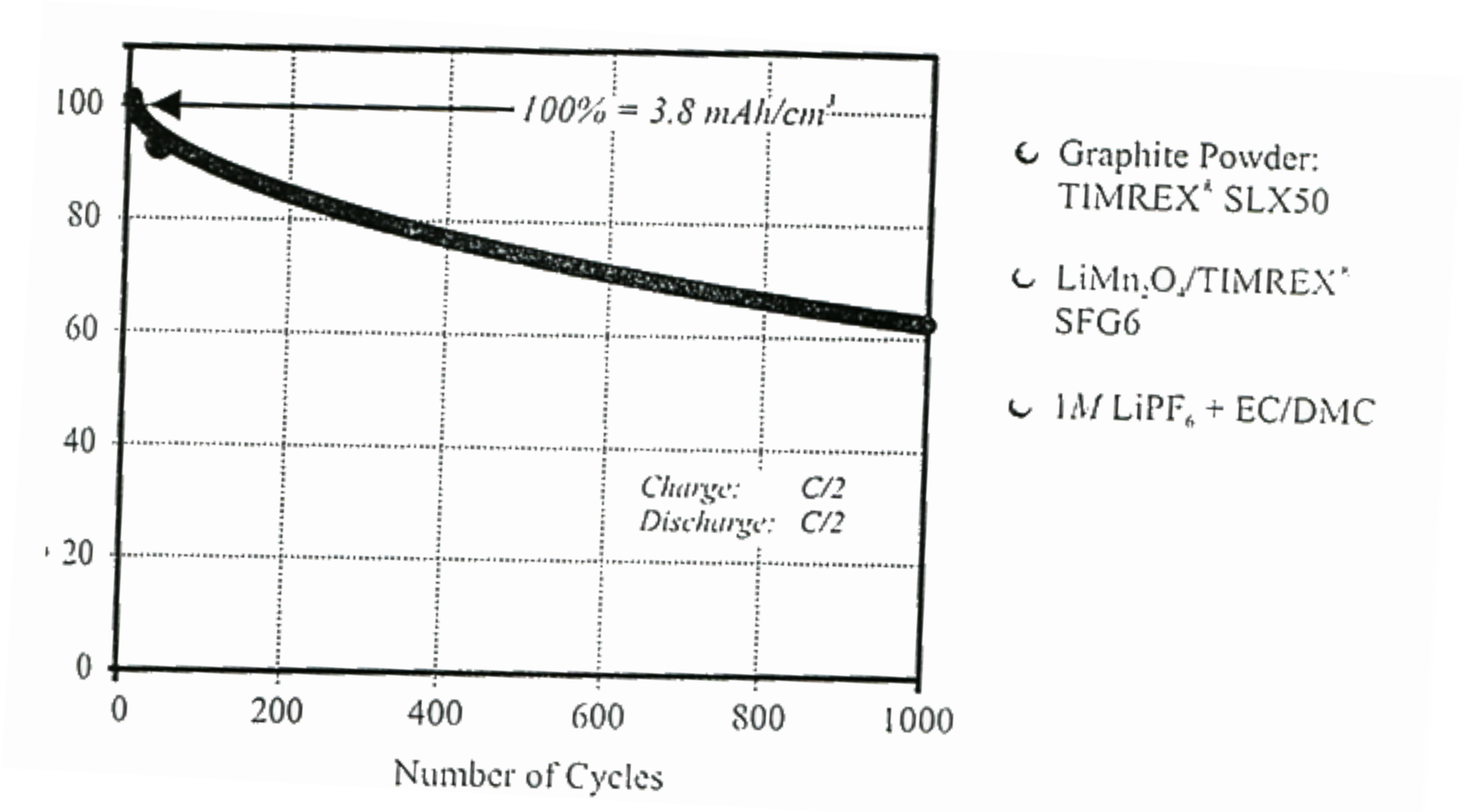


Specific power (W/kg of the oxide) of a $LiMn_2O_4$ electrode containing TIMREX®SFG6 as conducting additive

Left: specific power curves for discharge are plotted vs. time

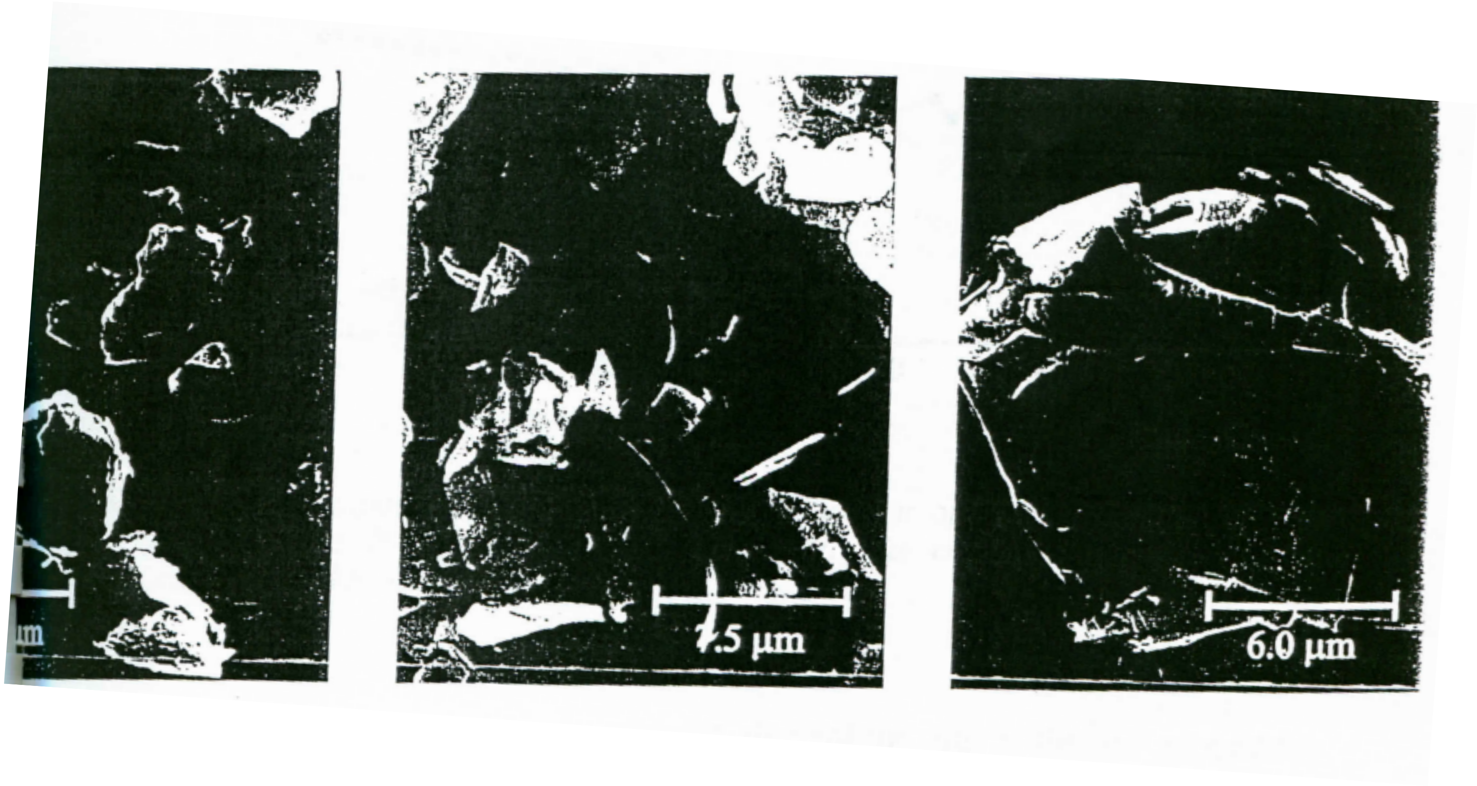
Right: Ragone diagram showing the relationship between the specific power and the available specific energy of the system

Lithium-ion or “Roching-chair” batteries



Electrochemical cycling performance of a coin cell containing a TIMREX® SLX50 negative electrode and a $LiMn_2O_4$/TIMEREX® SFG6 positive electrode (courtesy of PSI)

Lithium-ion or “Roching-chair” batteries



SEM pictures of TIMREX® graphites suitable as conductive additives from left to right: KS4, SFG6, MB15

Lithium-polymer Batteries

A number of laboratory studies have assessed the applicability of the rocking-chair concept to polymer-electrolyte-based cells.

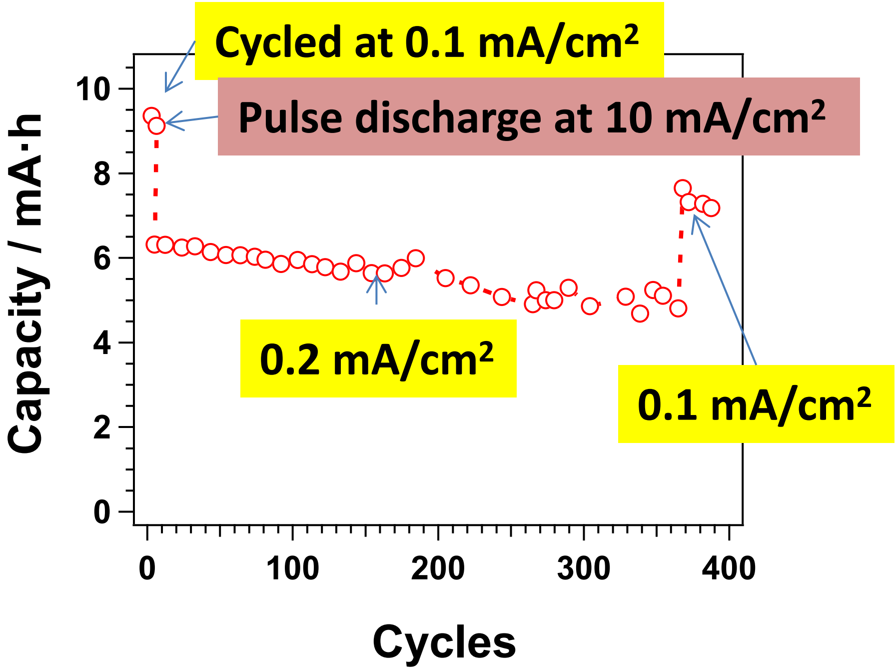
In particular, there have been a number of reports of cells based on the PAN-EC-PC gel electrolyte with various anode/cathode electrode couples.

Performance studies on cells of the

Li|PAN-EC-PC-based electrolyte|$LiMn_2O_y$ and carbon|
PAN-EC-PC-based-electrolyte|$LiNiO_2$

have indicated that capacity in both types declines with cycling.

Lithium-polymer Batteries



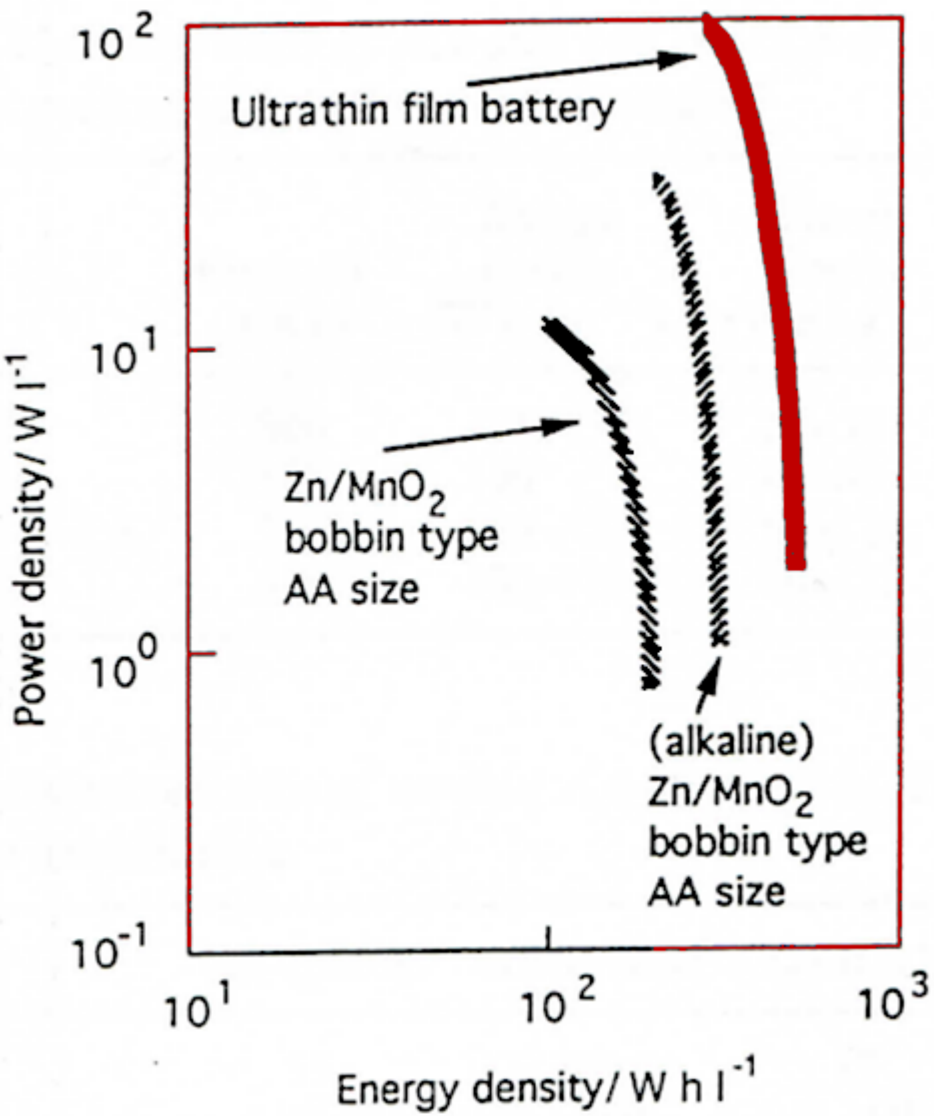
Discharge capacities as a function of cycle number of a carbon-LiNO$_2$ cell containing a PAN-based polymer electrolyte. The carbon electrode has a capacity of 9 mAh

For cells with a lithium anode, the capacity decay can be attributed mainly to passivation and loss of the lithium metal anode by its reaction with the electrolyte. For lithium-ion cells, cyclability has been shown to be reasonably impressive. A carbon/LiNiO$_2$ cell retains 85% of the initial discharge capacity after following the cycling regime of figure.

The reduction in capacity results from a rise in internal impedance, possibly associated with a reduction of the electrolyte on the carbon electrode.

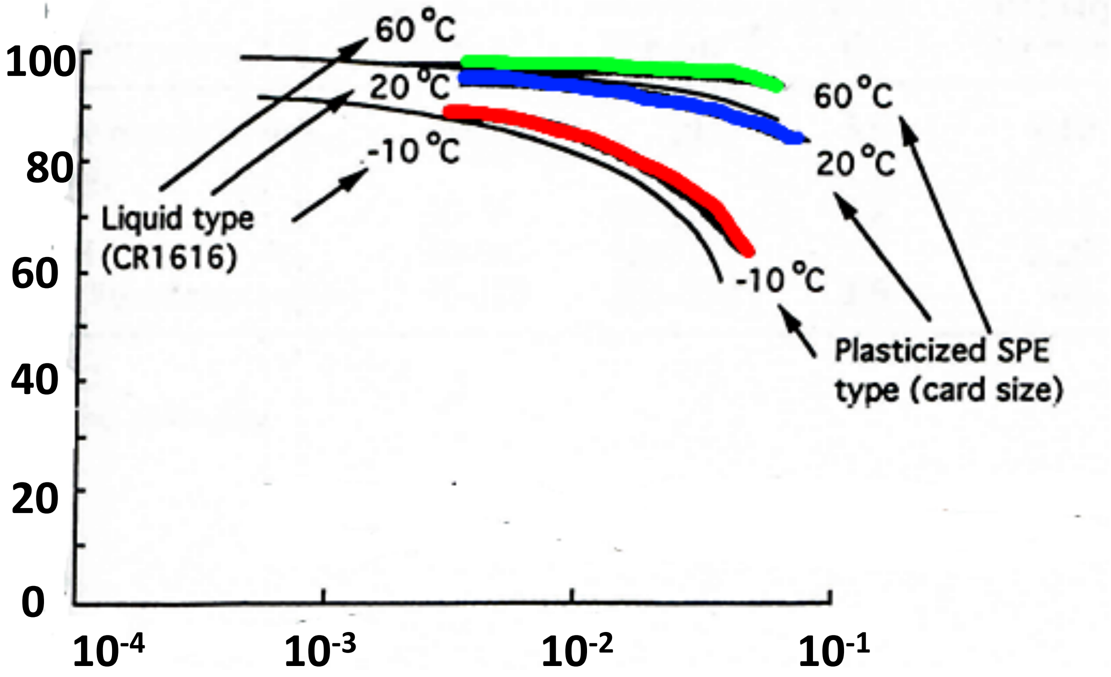
Other factors such as solvent co-intercalation, which is known to contribute to the decline in capacity of some organic liquid-electrolyte-based cells, have not yet batteries based on a plasticized polymer electrolyte, but a similar secondary battery is anticipated.

Lithium-polymer Batteries



Comparison of the performance of various primary batteries

Lithium-polymer Batteries



Discharge characteristics of a (primary) solid polymer electrolyte battery compared with those of a liquid battery, at various temperatures

Specifications of a commercial thin film primary lithium battery

Specification	Charcteristic value
Nominal voltage / V	3
Nominal capacity / mAh	150 (cutoff at 2.0 V)
Volumetric energy density / Whdm^{-3}	450
Weight / g	2.6

Lithium-polymer Batteries

Nominal characteristics of AA-size (48x13.5∅) secondary cells. The value for polymer electrolytes are estimated

	Ni-Cd	Ni-MH	Li-ion (RCT)	Li-polymer (est.)
OCV / V	1.3	1.3	3.0 – 3.6	2.5
Capacity / mAh	800	1100	500	450
Energy density / $Whdm^{-3}$	85 – 135	160	225 – 350	100 – 170
Energy density / $Whkg^{-1}$	30 – 50	60 – 80	90 – 120	70 – 120
Cycles	>1000	500	>1000	200
% loss per months	> 15	> 20	~8	< 1

Nominal characteristics of various AA-size primary and secondary lithium cells

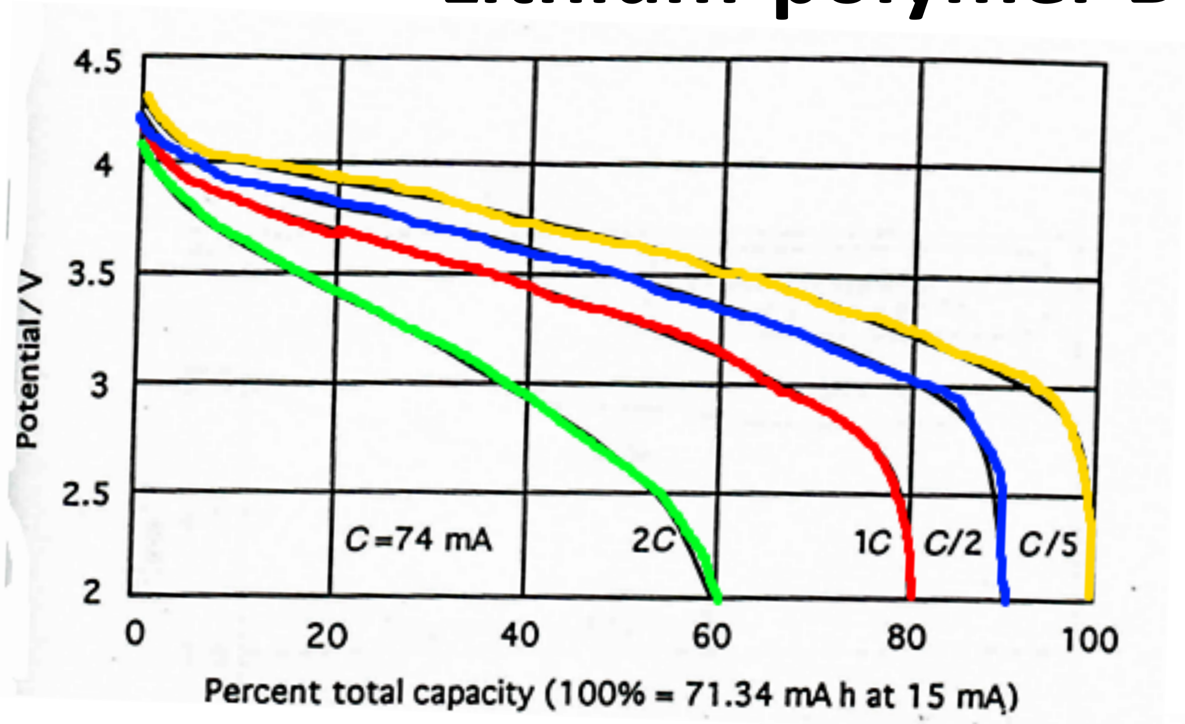
Characterisitic	Zn-Carbon[a]	Alkali-Mn[a]	Li-MnO2[a]	Ni-Cd[b]	Li-ion[b]
Weight / g	15	23	17	20	18
Energy / Wh	1.2	2.0	4.0	0.6	1.6
Energy density / Whkg^{-1}	80	86	235	30	90
Energy density / Whdm^{-3}	170	280	570	85	230

[a] **Primary cell** [b] **Secondary cell**

Typical performance characteristics of the Bellcore plastic Li-ion battery and other rechargeable battery technologies

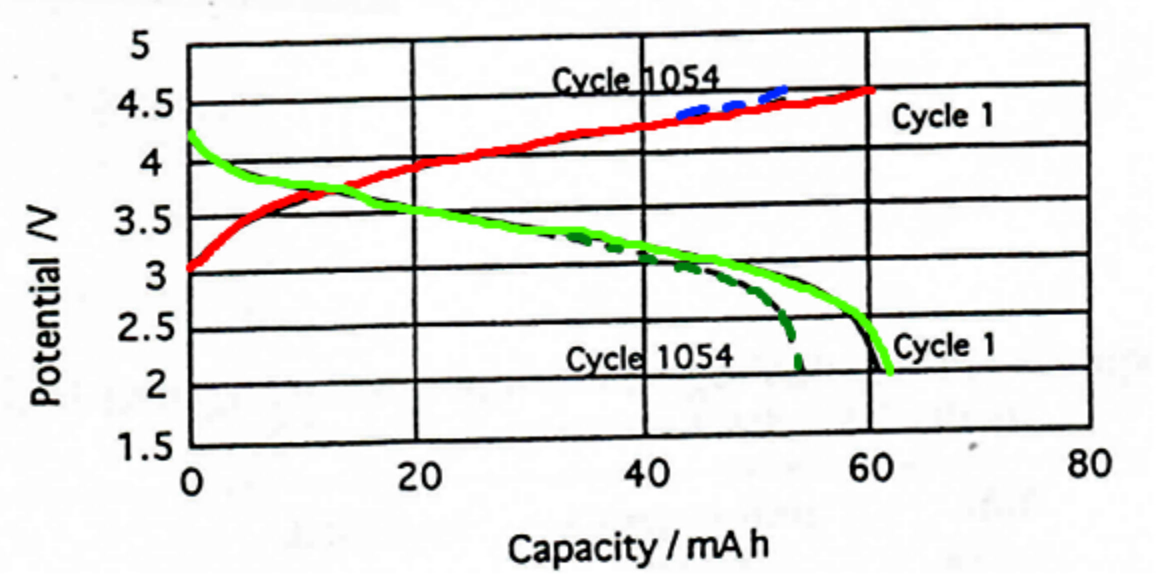
	Bellcore plastic Li-ion battery	Ni-Cd	Ni-MH	Li-ion (liq. Electrolyte)
OCV / V	3.6	1.2	1.2	3.6
Energy density / Whdm^{-3}	280	85 – 150	155 – 185	225 – 350
Energy density / Whkg^{-1}	110 (Excluding packaging)	30 - 55	50 – 80	90 – 120
Cycles	>1000	>1000	500	>1000
% Self discharge per months (at 20°C)	< 10	> 15	> 20	~ 8

Lithium-polymer Batteries

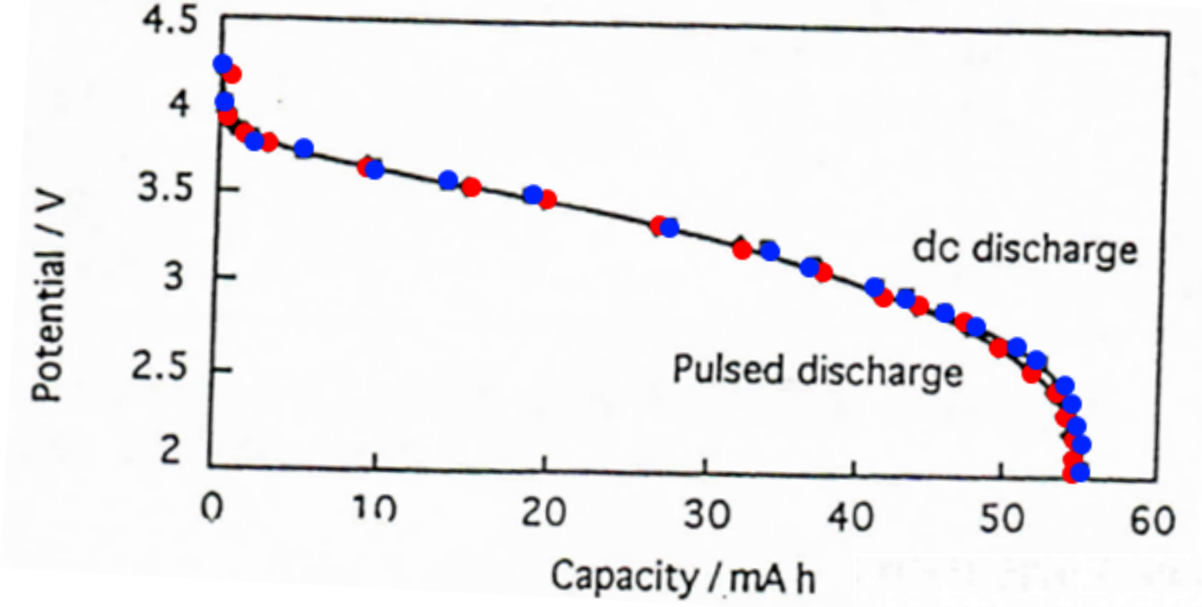


Constant-current discharge capacity at various rates of discharge at 23°C for a lithium-ion Solid State System TM battery (Reprinted with permission from Electronic Design, feb 13-17, 1995, copyright 1995, Penton Publishing Co.)

Charge and discharge cell cycle capacities at a C-rate of 74 mAh for a lithium-ion Solid State System TM battery (Reprinted with permission from Electronic Design, feb 13-17, 1995, copyright 1995, Penton Publishing Co.)

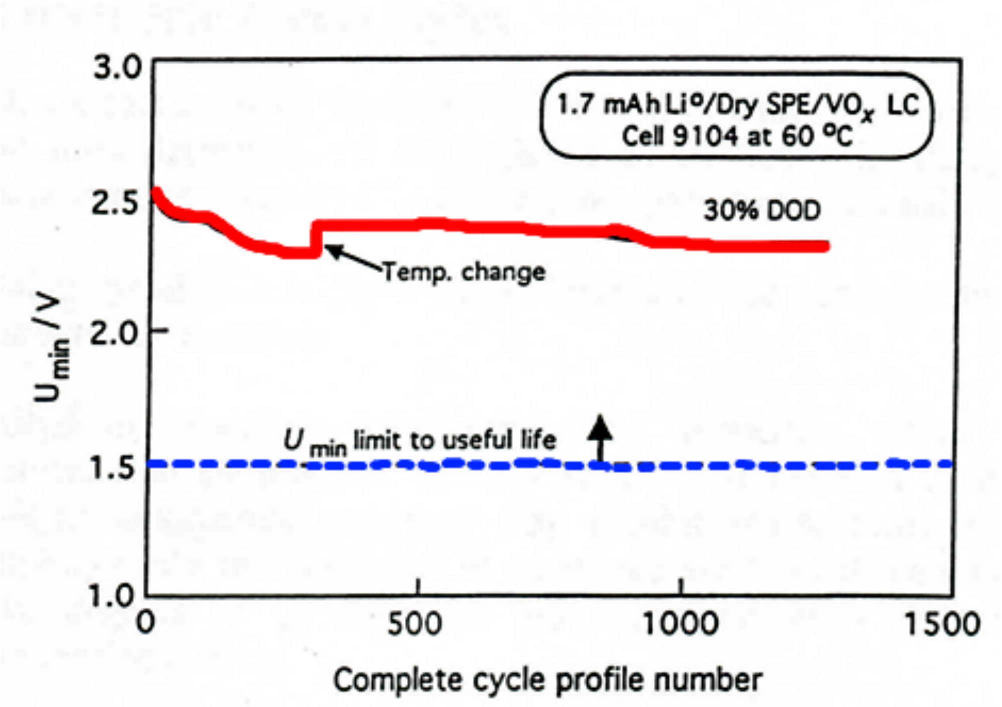


Lithium-polymer Batteries



Comparison of 200 Hz pulsed and dc discharge curves for a lithium-ion Solid State System TM battery (Reprinted with permission from Electronic Design, feb 13-17, 1995, copyright 1995, Penton Publishing Co.)

Wheelchair application: outdoor profile testing over three years



Lithium-polymer Batteries

Theoretical energy density, Mid-discharge Voltage and composition Range of some Li^+-insertion cathode systems

System	Ref.	Composition range	Mid-voltage / V	Specific energy / $Whkg^{-1}$
$cLi_xV_2O_5$	5	$0 < x < 1$	3.2	454
$aLi_xV_2O_5$a	5	$0.6 < x < 2$	2.8	541
$Li_xV_6O_{13}$	5	$0 < x < 3.6$	2.3	412
$Li_xCr_3O_8$	62	$1.5 < x < 3.3$ $0.6 < x < 3.6$	3.0 2.9	472 755
Li_xCoO_2	63	$0 < x < 0.64$	3.9	688
Li_xMoO_2		$0 < x < 1$	1.4	278
Li_xTiS_2		$0 < x < 1$	2.15	484
Li_xAlTiS_2b		$0 < x < 1$	1.9	349

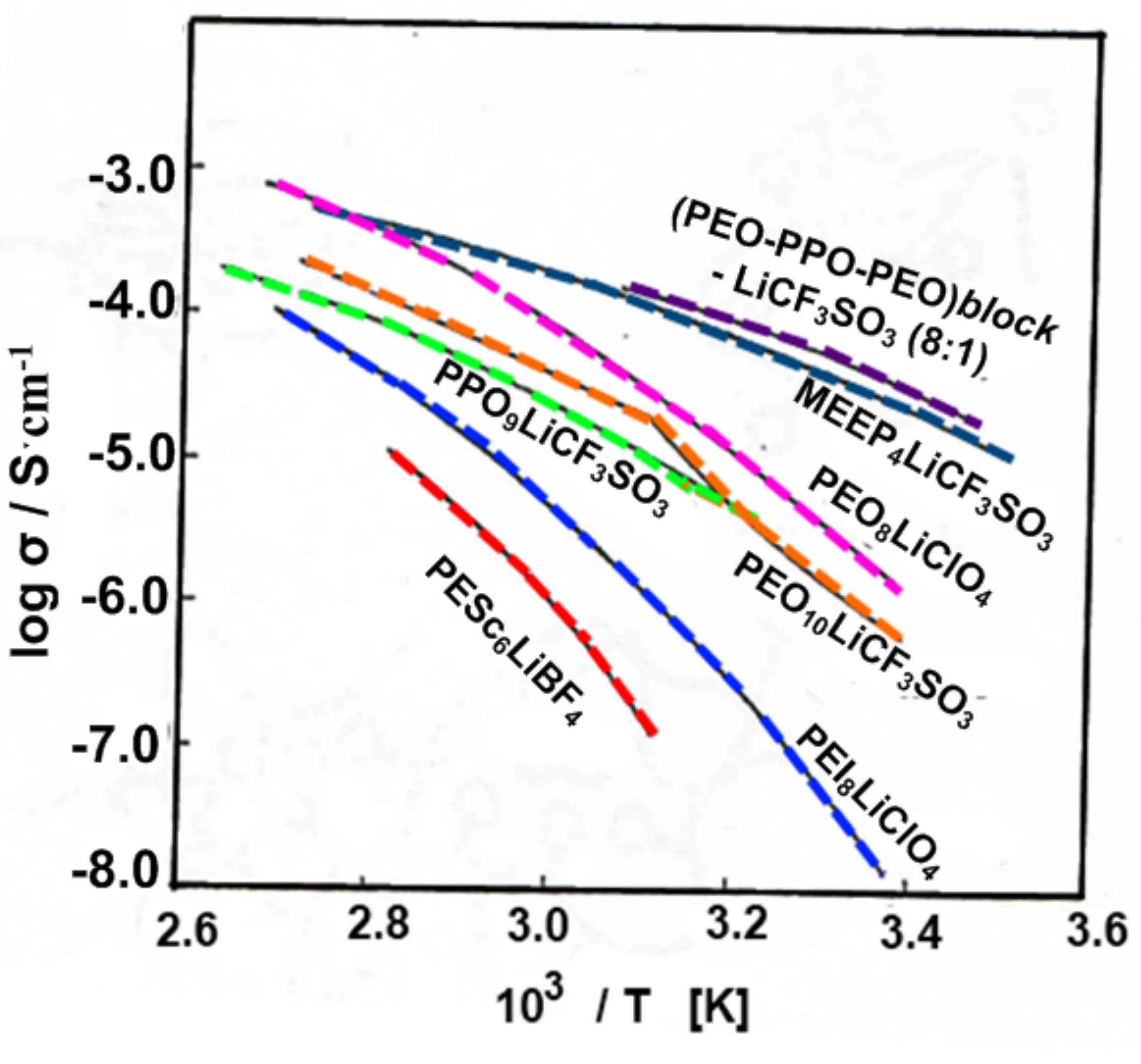
[a] Amorphous V_2O_5: 95% mol V_2O_5, 5 % mole P_2O_5

[b] LiAl: 50-50% mole

Polymeric Electrolytes

- ✓ One aspect common to all the above system is the irrelevance of ion association: the solid electrolytes are all single-ion conductors and, although molten salts may have more than one mobile species are essentially dissociated.
- ✓ Solid crystalline and glassy electrolytes have one particular disadvantage: they are hard, brittle materials.
- ✓ Polymeric materials have mechanical properties which should allow the construction of practical all-solid-state electrochemical cells. High molecular weight amorphous polymers may exhibit macroscopic properties that have attributes of a true solid but, at an atomic level, local relaxations provide liquid-like degrees of freedom that are not significantly different to those of a conventional liquid
- ✓ Polymers are not brittle, and so they are able to form good interfacial contacts with electrode materials and, more important, maintain these contacts under stressed such as the volume change associated with cell charging and discharging
- ✓ Ionic conductivities of $LiClO_4$ complexes are found to be of the order of 10^{-4} – 10^{-5} Scm^{-1}.

Polymeric Electrolytes



Conductivity vs temperature for some of the first studied polymer electrolytes.

PESc = poly(ethylene succinate),

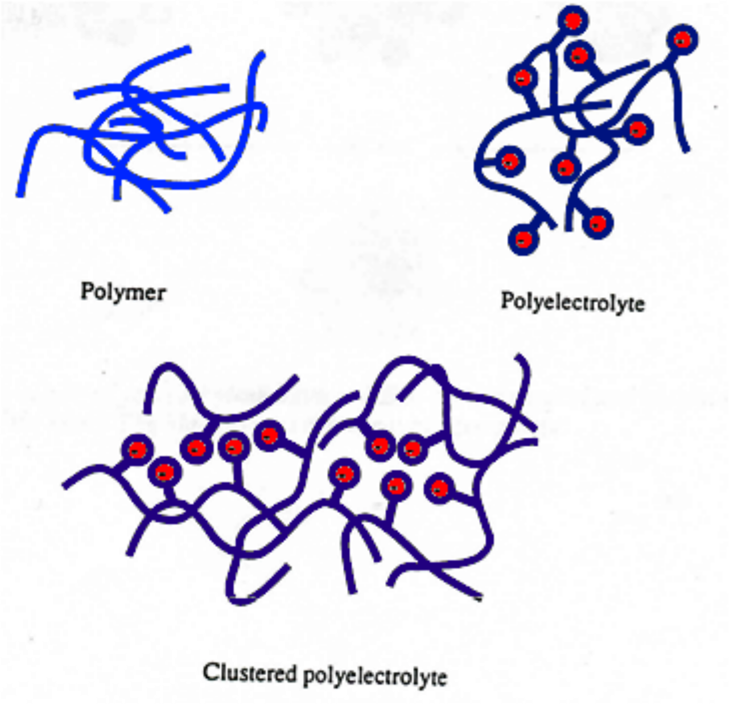
PEO = poly(ethylene oxide),

PPO = poly(propylene oxide),

PEI = poly(ethylene imine),

MEEP = poly(bis(methoxyethoxy) phosphazene)

Polymeric Electrolytes

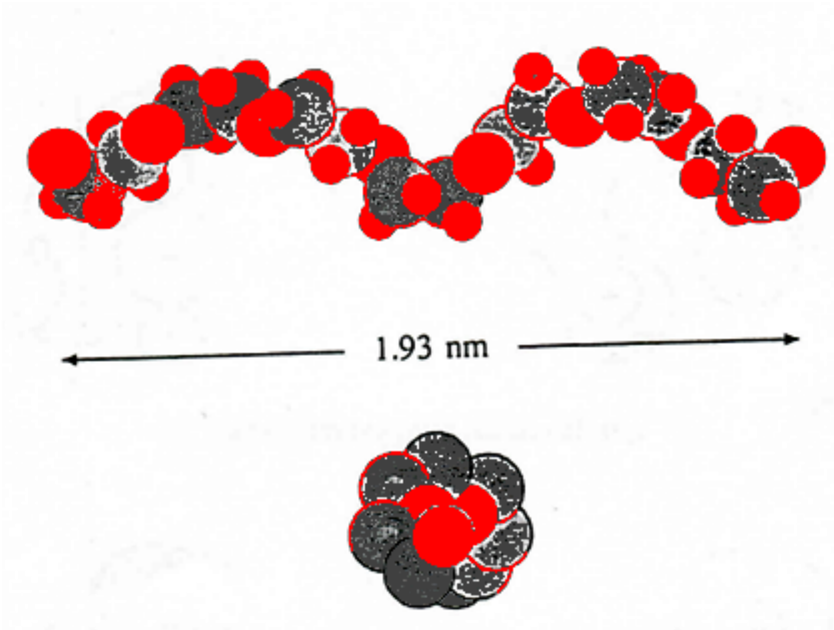


Representation of a simple polymer, a simple polyelectrolyte with anionic side-chain (e.g. poly(styrene sulfonate)) and a microphase separated system with anionic side-chains (e.g. NAFION®)

$-(CH_2CH_2O-)_n$ poly(ethylene oxide) PEO

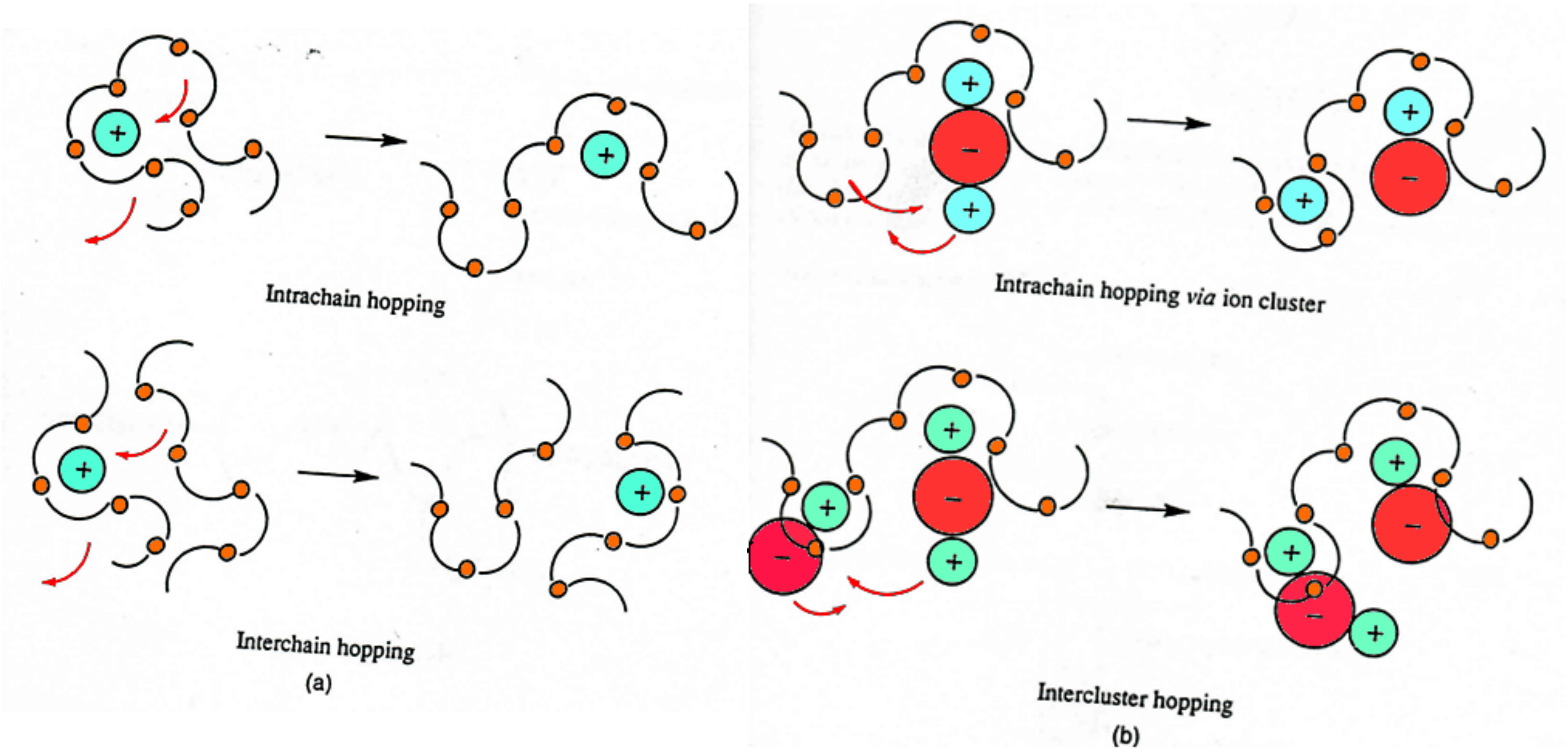
$-(CH_2CH_2(CH_3)O-)_n$ poly(propylene oxide) PPO

$-(CH_2CH_2NH-)_n$ poly(ethylene immine) PEI



Stucture of poly(ethylen oside), PEO, viewed parallel and normal to the axis of the helis. The black circles represent oxygen atoms

Polymeric Electrolytes



Intrachain hopping

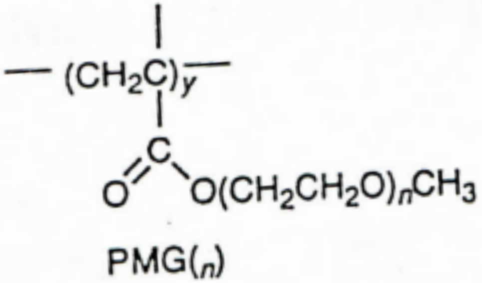
Intrachain hopping *via* ion cluster

Interchain hopping
(a)

Intercluster hopping
(b)

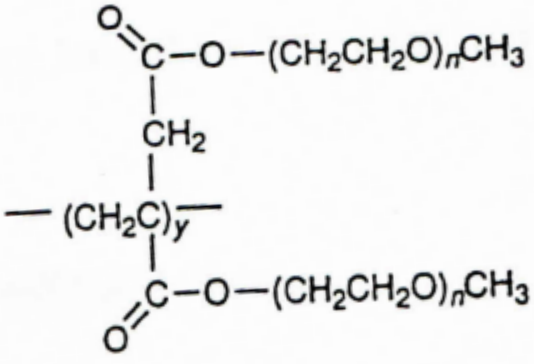
Representation of cation motion in a polymer electrolyte (a) assisted by polymer chain motion only, (b) taking account of ionic cluster contributions

Polymeric Electrolytes



PMG(n)

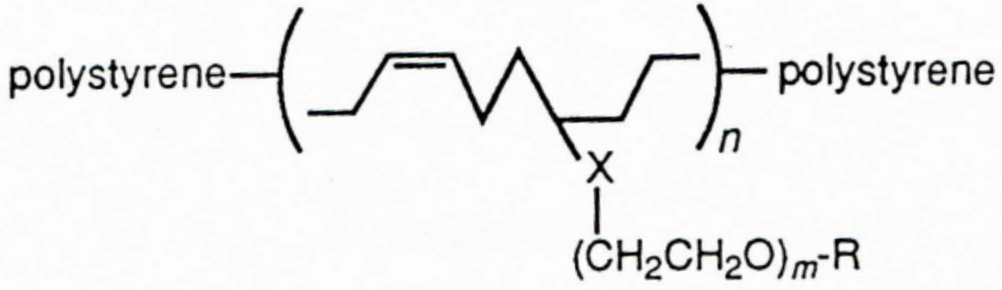
(a)

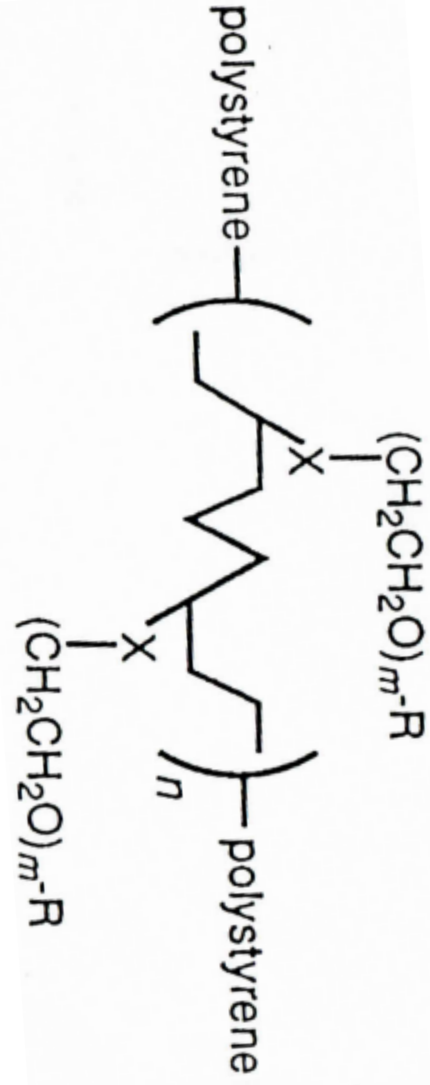


PMG(n)MI

(b)

Structure 1

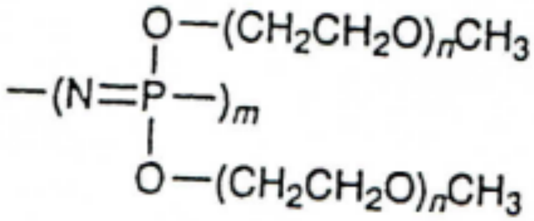




Styrene-butadiene-styrene ABA triblock polymer with a proportion of the C = C sites in polybutadiene replaced. The final polymer will contain a random distribution of a number of mono- and disubstituted structures

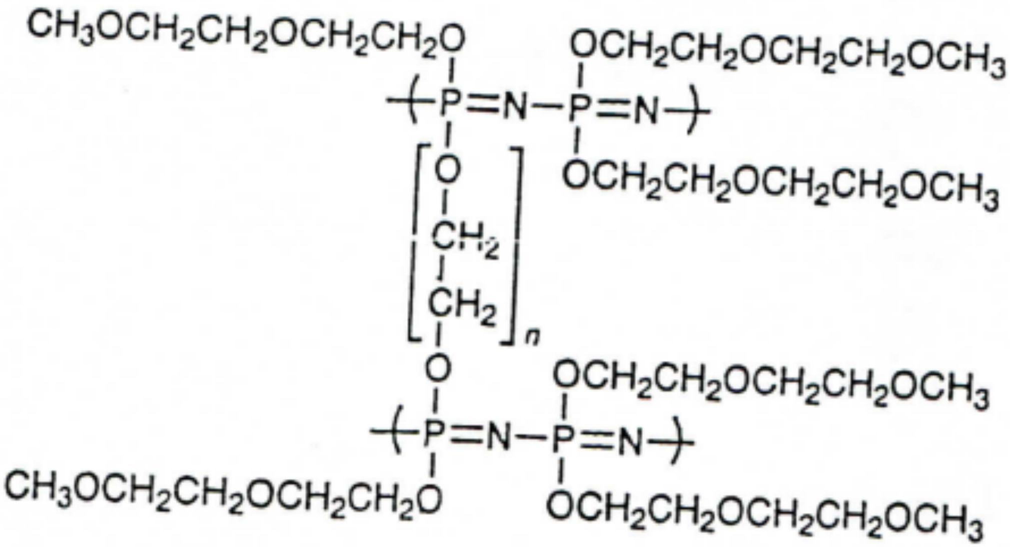
Polymeric Electrolytes

Polyether-linked MEEP

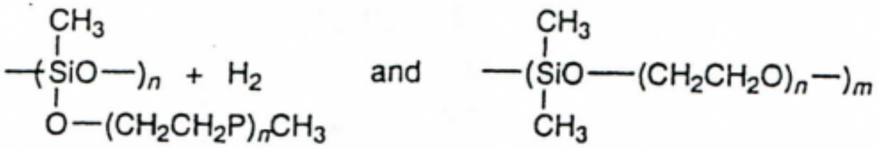


$$-(N{=}P[O-(CH_2CH_2O)_nCH_3]_2-)_m$$

Structure 2



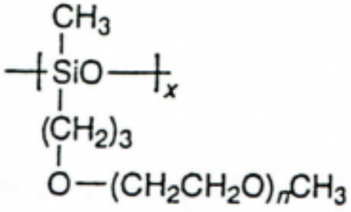
Polymeric Electrolytes



PMMS-*m*

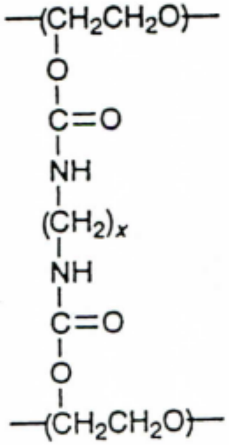
DMS-*n* EO
($n = 1,2,4,9$)

Structure 4

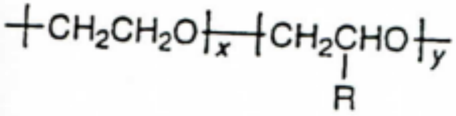


PAGS-*m*

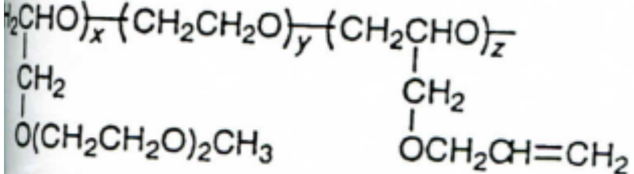
Structure 5



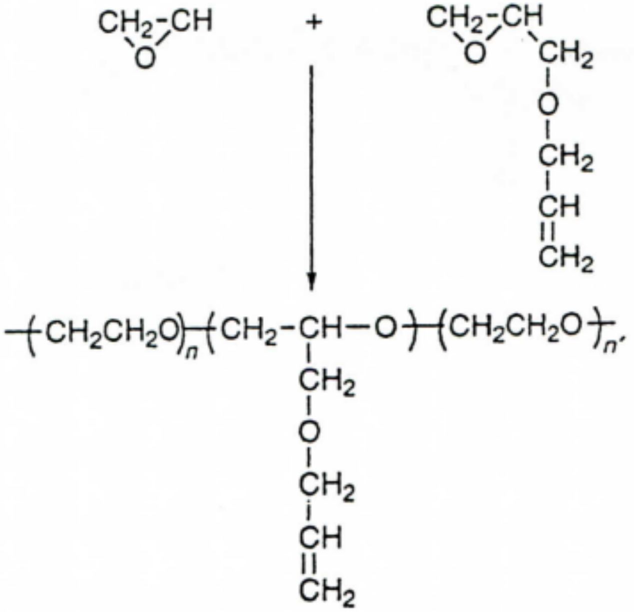
Structure 6



Structure 7

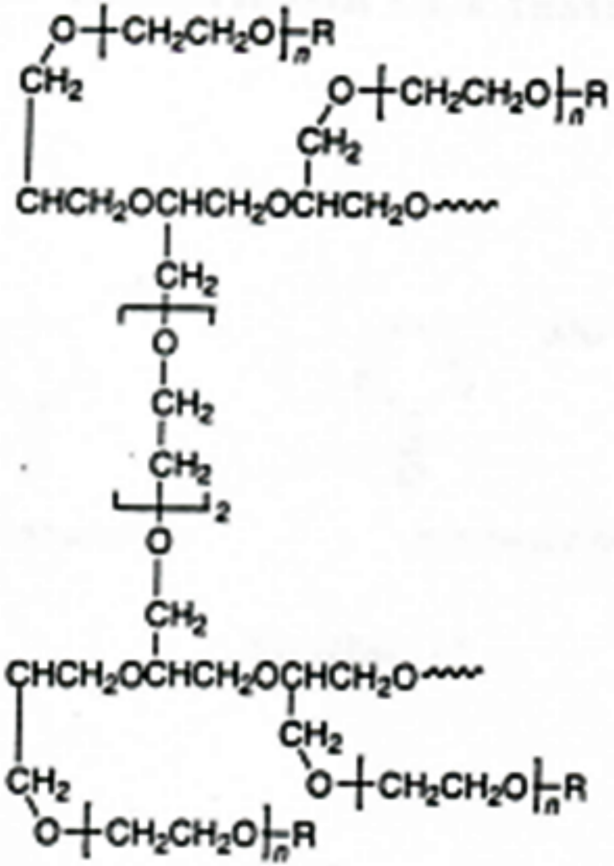


Structure 8



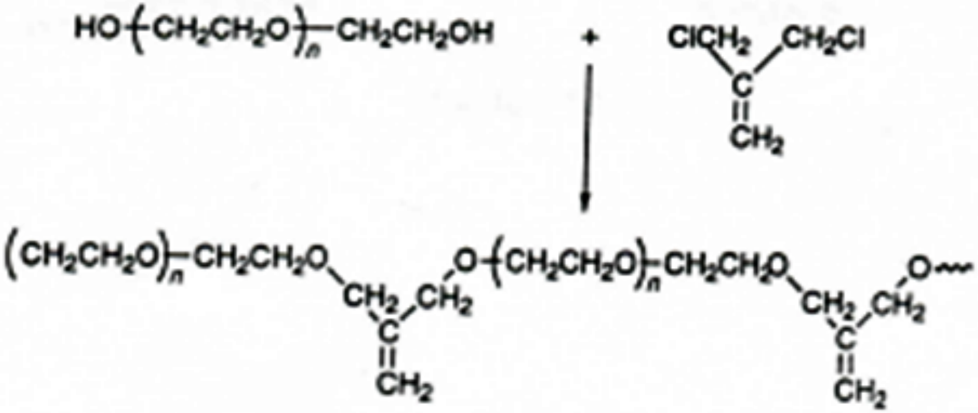
Scheme 1

Polymeric Electrolytes



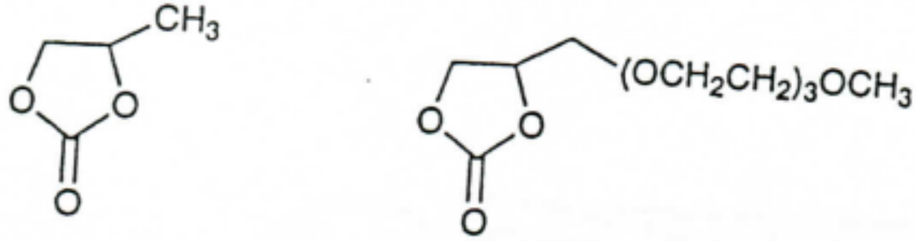
(9) R = Me, Et; $2 \leq n \leq 8$

Structure 9



Scheme 2

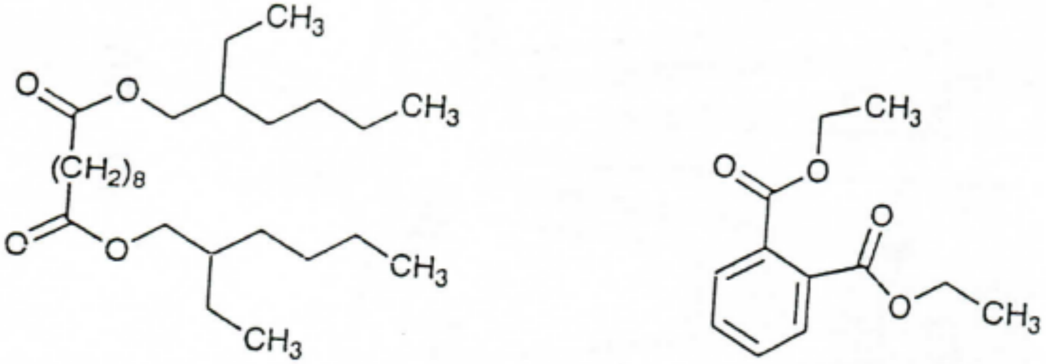
A New Generation of Plasticizer



propylene carbonate

modified carbonate

Structure 11



dioctyl sebacate
[bis(2-ethylhexyl) sebacate]

diethyl phthalate

Structure 12