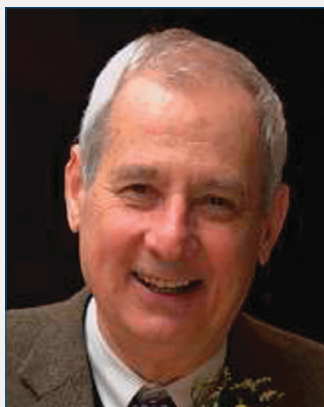




## LITHIUM BATTERIES

*È un grande onore, come socio della SCI e come direttore della rivista, ripubblicare l'introduzione di questo articolo sulle "Lithium Batteries" di Bruno Scrosati (presidente della SCI nel triennio 1996-1998), apparso nel 1997 su La Chimica e l'Industria, 79(4), 463, proprio in questo numero dedicato al Convegno di Salerno sui rapporti Industria-Accademia, nell'anno dedicato alla storia della nostra rivista per la celebrazione dei suoi 100 anni e nell'occasione dell'annuncio del premio Nobel per la Chimica recentemente attribuito a tre chimici stranieri "For development of lithium ion batteries", motivazione con lo stesso titolo di questo articolo. Le batterie al litio sono state oggetto della ricerca di Scrosati per molti anni con parecchie pubblicazioni, brevetti e collaborazioni con numerose industrie nazionali e straniere. Inoltre non dobbiamo dimenticare che le batterie sono utilizzate "nelle macchine elettriche, strumenti efficaci per migliorare l'area delle città", titolo, questo, di un altro articolo di Scrosati pubblicato nella nostra rivista nell'ottobre del 1998. La figura di Scrosati è emblematica per spiegare quelli che devono essere i rapporti fra Accademia e Industria.*

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The characteristics and performance of the most promising types of advanced batteries, i.e. the lithium metal, the lithium polymer and the lithium in batteries, are here briefly described and discussed. The present trends in our emerging technology strongly rely on portable electrical power sources such as electrochemical batteries. For instance popular electronic devices, e.g. cellular phones, camcorders and computers, need suitable batteries for their operation. Adequate batteries are also requested for promoting the wide commercialization of electric vehicles. These requests are not properly met by conventional batteries. The principal problem is that their electrode combinations have limited specific capacity (i.e. limited ampere-hours per gram of reactants) which is reflected in their relatively low energy density (i.e. limited watt-hours stored per weight or per volume of the battery). This is shown in Figure 1, which illustrates the relationship between gravimetric ( $\text{Whkg}^{-1}$ ) and volumetric ( $\text{Whdm}^{-3}$ ) energy density.

It is evident that conventional batteries, such as lead-acid or nickel-cadmium, are capable of providing only modest energy contents. Although systems with improved design and electrode configuration, such as the nickel metal hydride battery, may give somewhat higher energy density, it is clear that a major increase in energy content can only be achieved through the development of new, advanced batteries that are capable of at least doubling the energy values of the conventional ones. To achieve this goal the use of high capacity electrode materials is the essential factor. Alkali metals are the obvious choice research of new, high-energy, power sources appears today that directed to the development of lithium batteries. In fact, lithium is more easily handled than other alkali metals and, most significantly, it is the lightest and the most electropositive of the family. In its essential structure, a rechargeable lithium battery is formed by a lithium metal anode (hence the name *lithium battery*), a lithium ion conducting electrolyte and a lithium-ion-accepting cathode material. The latter is based on compounds having an open structure capable of accepting and releasing "x" number of lithium ions per mole. These materials are usually called "lithium intercalation cathodes. The overall electrochemical process of a lithium battery is schematically illustrated in Figure 2. During discharge it involves the dissolution of x lithium ions at the anode, their migration across the elec-

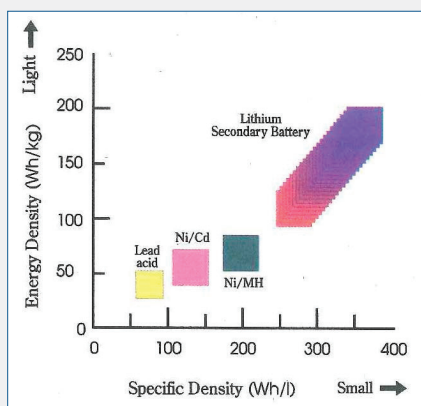


Figure 1 - Comparison of volumetric and gravimetric energy content of various types of rechargeable batteries

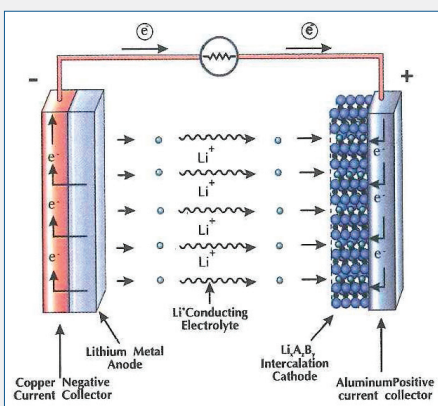


Figure 2 - Schematic illustration of the basic electrochemical process of a lithium battery

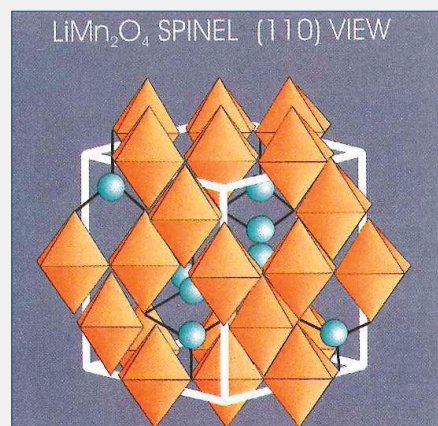
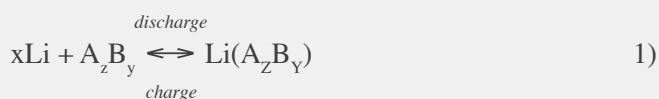


Figure 3 - Schematic view of the structure of spinel  $\text{LiMn}_2\text{O}_4$

trolyte and their insertion within the crystal structure of the host cathode compound, while the compensating electrons travel in the external circuit to finally be injected in the electronic band-structure of the same compound. The charge process is just the opposite. The electrochemical process can be then written as:



where  $\text{A}_z\text{B}_y$  is a generic intercalation cathode. Therefore, any liquid or solid material characterized by fast lithium ion transport can be used as an electrolyte medium for these batteries. Traditionally, the most common examples of electrolytes for lithium batteries are liquid solutions of lithium salts in aprotic organic solvent mixtures. [...] Beside liquid, also solid, i.e. crystalline or glassy compounds having vacancies or interstitial defects energetically favorable for  $\text{Li}^+$  transport and polymers, i.e. lithium ion conducting membranes, can be used as electrolytes in lithium batteries. Some typical examples of liquid and solid electrolytes of common use in lithium batteries are listed in Table 1. The most popular Li intercalation cathode compounds employed in lithium batteries (i.e. the  $\text{A}_z\text{B}_y$  compound in Eq. (1)) are vanadium oxides, e.g.,  $\text{V}_6\text{O}_{13}$  and  $\text{V}_2\text{O}_5$  titanium disulphide,  $\text{TiS}_2$ , molybdenum disulphide  $\text{MoS}_2$  and manganese oxide,  $\text{MnO}_2$ . The amount of lithium which can be reversibly intercalated in the various cited compounds, sometimes called the “intercalation level”, and which determines the capacity of a given battery, varies from case to case. Very interesting intercalation cathode materials for lithium batteries are man-

ganese dioxide-based compounds. Manganese dioxide is a cheap, readily available and is used world-wide as a solid cathode for primary liquid cells. During the last years remarkable progress has been made in the development of spinel-type manganese dioxide for rechargeable cells. Of particular interest is the  $\text{LiMn}_2\text{O}_4$  compound which is available in two forms, i.e. a high voltage (about 4 V vs. Li),  $\text{Li}_{(1-x)}\text{Mn}_2\text{O}_4$  form which is capable of releasing lithium ions, and a low voltage (about 3 V vs. Li),  $\text{Li}_{(1+x)}\text{Mn}_2\text{O}_4$  form which is capable of accepting lithium ions. The 4 V modification is used for lithium ion batteries [...] while the 3 V modification is used for lithium metal batteries. The  $\text{LiMn}_2\text{O}_4$  compound has a cubic spinel structure in which the  $(\text{Mn}_2\text{O}_4)$  framework possesses a 3D interstitial space via face sharing octahedra and tetrahedra. This provides a conducting pathway for  $\text{Li}^+$  ions which remains intact for both lithium insertion and extraction over the  $-1 < x < 1$  composition range (Figure 3).

Electrolyte	Status	Average conductivity ( $\text{Scm}^{-1}$ )	Applications
$\text{LiAsF}_6\text{-2Me-THF-EC}$	liquid	$8 \times 10^{-3}$	lithium metal
$\text{LiCF}_3\text{SO}_3\text{-PC-1,2DME}$	liquid	$6 \times 10^{-3}$	lithium metal
$\text{LiPF}_6\text{-EC-DMC}$	liquid	$6 \times 10^{-3}$	lithium ion
$\text{PEO-Li}(\text{CF}_3\text{SO}_2)_2\text{N}$	solid	$10^{-4}$ (80 °C)	lithium polymer
$\text{PEO-LiCF}_3\text{SO}_3+\gamma\text{-LiAlO}_2$	solid	$10^{-4}$ (80 °C)	lithium polymer
$\text{PMMA-PC-EC-LiClO}_4$	solid	$5 \times 10^{-4}$	lithium polymer
$\text{PVDF-HFP}(\text{+LiPF}_6\text{-EC-DMC})$	solid-liquid	$10^{-3}$	lithium ion plastic
$\text{PMMA-EC-DMC-LiClO}_4$	solid	$10^{-3}$	lithium ion plastic

Table 1 - Basic properties at room temperature of some examples of liquid, solid and polymer electrolytes for lithium batteries