



## Review Paper

# Cathode Materials for Solid State Microbatteries – A Case Study

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## Abstract

*As the general tendency of all advanced technologies is towards miniaturization, it is evident that the future development of batteries is aimed at smaller dimensions with higher-energy densities. A microbattery is an energy conversion/storage device, designed and built with microelectronics thin film fabrication technologies with footprints of the order of 50-100  $\mu\text{m}^2$  having capabilities to provide currents of the order of 100-200  $\mu\text{A}/\text{cm}^2$  with storage capacities in the range of 70-200  $\mu\text{Ah}/\text{cm}^2$ . Lithium rechargeable batteries are gaining more importance now a days because of their capacity compared with conventional rechargeable systems and due to their wide potential use, ranging from portable devices to heavy electric vehicles. The use of transition metal oxides as intercalation cathodes has turned the lithium power sources into the current generation. Lithium transition metal oxides have received significant attention due to their industrial applications especially in rechargeable lithium-ion batteries. These materials are applied on the cathode side where Li is, respectively extracted and stored during the charge-discharge cycle of the battery.*

**Keywords:** Micropower, lithium batteries, thin film microbattery, cathode materials,  $\text{LiCoO}_2$ .

## Introduction

The energy conversion, storage and distribution are the important concerns of our civilization in order to meet the challenges of global warming and finite nature of the fossil fuels. In response to the needs of the modern society and emerging technological advancements, it is now essential that new, low cost and environment friendly energy conversion and storage systems are to be developed. An idea of the quantitative importance of energy storage devices (batteries) in use can be given by the observation that their number is of the order of magnitude of the world population, a few billion, increasing every minute. Even if some of the remote African countries are not yet well equipped, every individual possesses, or uses, at least 10 batteries, if not more: cars, flash lamps, watches, radios, cellular telephones, credit cards, and all kinds of electronic devices. As the general tendency of all advanced technologies is towards miniaturization, it is evident that the future development of batteries is aimed at smaller dimensions with higher-energy densities. This is valid for all envisaged applications from power plants, electric cars, through portable electronics, to high-density-integrated circuits. For 200 years, since the discovery of Volta, the evolution has been slow, because of the nature of the electrochemical cell itself. A breakthrough has occurred only recently with the introduction of solid-state battery where a factor of 10 is gained in the energy density. The development of solid-state batteries parallels the development of semiconductor electronics. Today's tendency is to create solid-state integrable microbatteries that are compatible with semiconductor technologies. Such integrated microbattery compatible with the dimensions of

micro-devices will act as a source of power for many single components in integrated circuits and devices, which avoids electrical conduction leaks, inevitable power losses, cross talking and allows three dimensional integration.

## Solid-state Batteries

In a solid-state battery, the electric charge transport is assumed by a single type of ions, a cation  $\text{A}^+$ , while the anion is immobilized in the crystal lattice. The electrolyte is a solid fast ion conductor. The blocking of the anions prevents passivation, corrosion and solvent electrolysis reactions. Consequently there is no gas formation. It is therefore possible to design totally sealed batteries, eliminating the deterioration of the electrolyte and the electrodes by the outside environment. Under these conditions, the electrolyte can co-exists with couples which are highly reducing at the negative electrodes and highly oxidizing at the positive electrode. In such systems much higher energy densities can be achieved.

## Solid-state primary lithium batteries

The lithium-iodine battery has been used to power millions of cardiac pacemakers since its introduction in 1972. The lithium-iodine has established a record of reliability and performance unsurpassed by any other electrochemical power source. This battery has a solid anode of lithium and a polyphase cathode of poly-2-vinylpyridine which is largely iodine (at 90% by weight). The solid electrolyte is a thin  $\text{LiI}$  film. The cell has an open-circuit voltage of 2.8 V and the energy density is 100-200 Wh/kg. These batteries have extended system lives of 10 years

for 150-250 mAh capacities. Solid-state primary batteries can provide generally very long-life operation at low currents. Other example of such batteries is the lithium-glass batteries whose envisaged applications are mainly as power sources in electronic computers for CMOS memory back up.

### Solid state secondary lithium batteries

The solid-state rechargeable batteries are with very low capacity, generally of the order of mAh, and yet a large research and developmental effort is engaged, the target is the CMOS memory back up. Variety of solid electrolytes and intercalation cathode materials are used. The general schema of the cell is solid lithium anode, fast-ion conducting glass electrolyte and layered intercalation compound cathode. An example is the cell  $\text{Li}/\text{LiBF}_4 - \text{PC}/\text{CF}_x$  with a cell voltage of 2.8 V and energy density 320 Wh/kg.

Among the various existing technologies, rechargeable lithium ion cells are the key components of the portable, entertainment, computing and telecommunication equipment required for today's information-rich, mobile society as shown in figure-1. The motivation for using a battery technology based on lithium as anode relied initially on the fact that Li is the most electropositive (-3.04 V versus standard hydrogen electrode) as well as the lightest (equivalent  $M = 6.94 \text{ g/mol}$ , and specific gravity  $\rho = 0.53 \text{ g/cm}$ ) metal, thus facilitating the design of storage systems with high energy density. The advantage of

using Li metal was first demonstrated in the 1970s with the assembly of primary Li cells. Owing to their high capacity and variable discharge rate, they rapidly found applications as power sources for watches, calculators or for implantable medical devices. Over the same period, numerous inorganic compounds were shown to react with alkali metals in a reversible way. The discovery of such materials, which were later identified as intercalation compounds, was crucial in the development of high-energy density.

Recently, thin films of functional materials including oxide ceramics have become important for use in many electronic, photonic, magnetic, ionic, etc., devices. Most of them have been fabricated through the so-called highly technical processing routes that require a high consumption of energy (such as physical vapor deposition<sup>1</sup>, chemical vapor deposition<sup>2</sup>, dip coating with firing<sup>3</sup>). However, we must consider also total environmental load of these processings in addition to their capability. The total energy consumption among all the processing routes should be the lowest in aqueous systems, because a much larger energy is necessary to create a melt, vapor or gas, or plasma than to form an aqueous solution at the same temperature<sup>4</sup>. Fabrication of these materials as thin film cathodes for application in all solid state microbatteries has been another interesting field of research owing to the miniaturization and the reduced power consumption of many kinds of electronic devices.

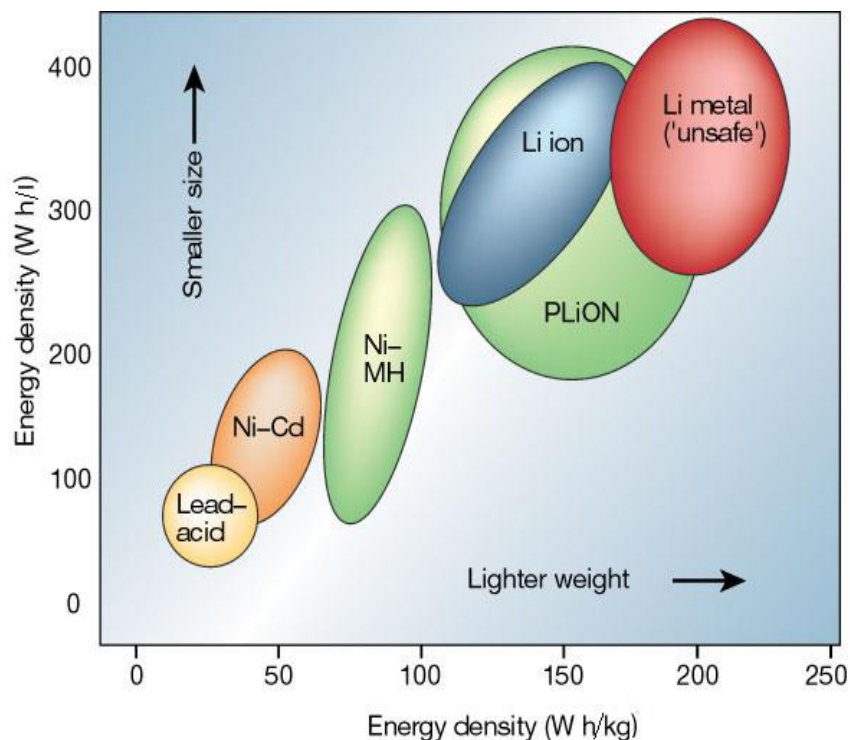


Figure- 1  
Comparison of the different battery technologies in terms of volumetric and gravimetric energy density

The lithium battery industry is undergoing rapid expansion, now representing the largest segment of the portable battery industry and dominating the computer, cell phone, and camera power source industry. However, the present secondary batteries use expensive components, which are not in sufficient supply to allow the industry to grow at the same rate in the next decade. Moreover, the safety of the system is questionable for the large scale batteries needed for hybrid electric vehicles (HEV). Another need is for a high-power system that can be used for power tools, where only the environmentally hazardous Ni/Cd battery presently meets the requirements.

A battery is a transducer that converts chemical energy into electrical energy and vice versa. It contains an anode, a cathode, and an electrolyte. The anode, in the case of a lithium battery, is the source of lithium ions. The cathode is the sink for the lithium ions and is chosen to optimize a number of parameters. The electrolyte provides for the separation of ionic transport and electronic transport, and in a perfect battery the lithium ion transport number will be unity in the electrolyte. The cell potential is determined by the difference between the chemical potential of the lithium in the anode and cathode, the electromotive force (EMF) is due to the potential difference between the metal and the intercalation material, which are characterized by the work functions  $\phi_m$  and  $\phi_s$ :

$$EMF = \phi_m - \phi_s = E_{F(s)} - E_{F(m)} = V_{oc}$$

Where  $V_{oc}$  is the open-circuit voltage

The total energy available for the discharge in a battery is:

$$\Delta G = nFV_{oc}$$

Where ' $\Delta G$ ' is the Gibb's free energy, ' $n$ ' is the number of transferred electrons and ' $F$ ' is the Faraday constant (96487 C/mol).

The energy theoretically available in an electrochemical generator through the discharge process is:  $E_{th} = xnFV_{oc}$ ,

Where ' $x$ ' is the molar quantity involved in electrochemical reactions during discharge.

The specific energy density is the energy that can be derived per unit weight of the cell (or sometimes per unit weight of the active electrode material). It is the product of the specific capacity and the operating voltage in one full discharge cycle. Both the current and the voltage may vary within a discharge cycle and thus the specific energy derived is calculated by integrating the product of current and voltage over time.

The theoretical capacity of a battery is the quantity of electricity involved in the electrochemical reaction. It is denoted by  $Q$ .

The capacity is usually given in terms of mass:  $Q = \frac{nF}{M_r}$

Where ' $n$ ' is number of electrons transferred per mole of reaction, ' $F$ ' is the Faraday's constant and ' $M_r$ ' is the Molecular Mass. This gives the capacity in units of Ampere-hours per gram (mAh/g).

The lithium ions flow through the electrolyte whereas the electrons generated from the reaction,  $Li = Li^+ + e^-$ , go through the external circuit to do work. Thus, the electrode system must allow for the flow of both lithium ions and electrons. That is, it must be both a good ionic conductor and an electronic conductor.

## Microbatteries

With the advent of micro-electromechanical systems (MEMS)<sup>5-9</sup>, micro-machines, micro-systems, integrated passive components and low power electronics for applications such as thermal or pressure meters, acceleration detectors, light detectors, sound monitors, sensors, micro/nanostructures for various types of functionalities aimed at miniaturization of spacecraft components, there has been a tremendous pressure on the development of ultra high energy density and power density sources of matching configuration to meet the requirements of micro/nano-spacecraft applications. Battery engineers, researchers and technologists are contemplating on systems of the size of a grain of sand or a red blood cell and there appears to be a significant progress in the study of thin films as materials for energy conversion and storage. Hence, the technological interest was to develop long lasting, high specific energy thin-film batteries that can be used as an integral part of the microelectronic circuit. Construction of a power source and a circuit on the same chip or substrate by employing a simple integrated battery or a distributed power supply is possible by fabricating the battery in thin film form which fulfills the interest for further integration of microelectronic technology. Batteries of the size of microelectronic devices, less than 5  $\mu m$  thick, are now being developed and built, using thin film deposition technologies, that are compatible with integrated circuits. They will be used in future as micro-devices, micro-sensors, integrated circuits and very large-scale integration (VLSI). An integrable microbattery compatible with the dimensions of micro-devices will act as a source of power for each single component in integrated circuits. Such microbatteries are used in VLSIs to back up semiconductor memory devices: dynamical random-access memories (DRAMs) incorporating metal-oxide semiconductor field effect transistors (MOSFETs)<sup>10</sup>. Today, the CMOS is the most common DRAM element combining both n- and p- channel MOS devices. The reason why microbatteries are appropriate to power CMOS memories is that these devices consume significant current only during switching from the logic state to another. When the leakage currents of the MOSFETs are only nano-amperes per devices, a small lithium primary battery can backup CMOS memories for many years. The fabrication technology of such microbatteries is perfectly compatible with the technologies of building the VLSIs.

For the same reasons solid-state microbatteries would be pertinent for emerging and future semiconductor devices and systems. Examples are the quantum well lasers which can be operated at low currents and the neural networks in their electro-optic implementations. If VLSIs are to operate at low temperature the possibility to use superconducting interconnects raises the probability of higher speeds and lower power requirements of possible relevance to microbatteries. Hybrid circuits involving Josephson junctions with very high-speed capabilities can also be powered with microbatteries.

A microbattery is an energy conversion/storage device, designed and built with microelectronics thin film fabrication technologies with footprints of the order of  $50\text{-}100\ \mu\text{m}^2$  having capabilities to provide currents of the order of  $100\text{-}200\ \mu\text{A}/\text{cm}^2$  with storage capacities in the range of  $70\text{-}200\ \mu\text{Ah}/\text{cm}^2$ . The advantages offered by thin-film microbatteries for on-chip power applications include: (1) manufacturing techniques similar to those used for microelectronics devices, enabling integration with the electronic circuit board, (2) the use of an extremely thin electrolyte layer of relatively poor conducting ionic conductors such as glassy solid electrolytes and (3) the ability to construct the microbattery in any desired two-dimensional shape. Such microbatteries are expected to provide localized low-power supply for the memory protection. They replace those capacitors that are commonly used external to the microelectronic device. The substitution of the capacitors with microbatteries as a backup power unit will not only offer significant advantages in terms of weight and volume (batteries have  $\sim 20$  times the specific energy compared to capacitors) but also pave the way for advanced memory storage devices such as self powered CMOS memories and RAMS.

### Microbattery structure

A solid state battery would be a microbattery operating as a solid state device where the positive charge is transported by small ions diffusing through a perfect electronic insulator and the negative charges are transported by electrons injected from the external circuit. Thus a solid state battery has three components and is shown in figure-2. The first is an ion source, lithium metal and the second is a fast ion conductor which should be as good an electrical insulator as possible to avoid electrical leakage while the battery is not in use, which would shorten its lifetime. The third component is an electron exchanger formed from an insertion material, into which the lithium ions penetrate during the discharge and are neutralized by the free electrons populating the conduction band of the insertion compound. The cathode material is therefore a mixed ionic-electronic conductor and its performance will depend on the mobility of both ions and electrons.

Lithium rechargeable batteries are gaining more importance now a days because of their capacity compared with conventional rechargeable systems and due to their wide potential use, ranging from portable devices to heavy electric vehicles. The use of transition metal oxides as intercalation cathodes has turned the lithium power sources into the current generation. Lithium transition metal oxides (LTMOs) such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$  have received significant attention due to their industrial applications especially in rechargeable lithium-ion batteries. These materials are applied on the cathode side where Li is, respectively extracted and stored during the charge-discharge cycle of the battery.

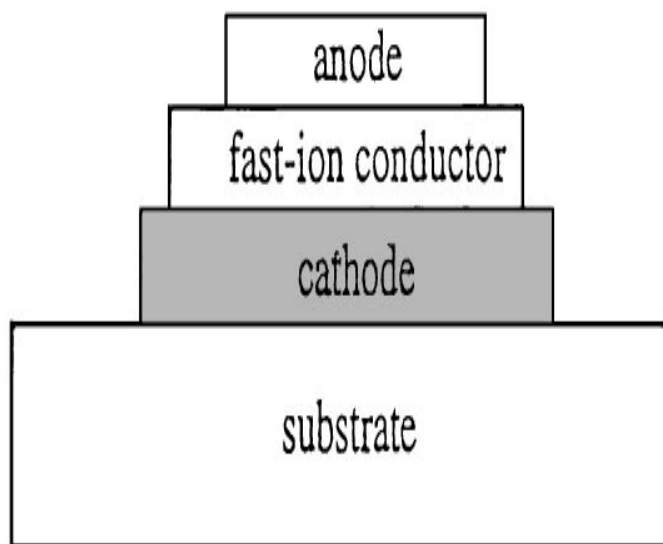


Figure-2  
Schematic representation of a solid-state microbattery

**Cathode materials are designed based on:** High cell voltage (large free energy of reaction), High cell capacity (wide compositional range) High rate (high diffusivity of Li guest) Long cycle life (minimum structural change) High power density (good electronic conductivity)

Candidate cathode materials for room temperature operation are the lithium-3d-metal oxides  $\text{LiMO}_2$ , where M stands for Mn, Ni, Co or a combination of these elements. Characteristics of the cathode materials for lithium battery are presented in table-1. Among these candidates  $\text{LiCoO}_2$  offers advantages like structural stability, high power density, high lithium diffusion velocity in the host and ease of preparation in film form. Its main disadvantage is the high price of cobalt.

Table-1

Characteristics of the cathode materials for lithium battery

Cathode	Theoretical Capacity (mAh/g)	Average Voltage (V)	Energy density (mWh/g)
$\text{LiCoO}_2$	274	3.6	986
$\text{LiNiO}_2$	275	3.6	990
$\text{LiMn}_2\text{O}_4$	148	3.8	562
$\text{LiMnO}_2$	286	3.2	914

### Lithium cobalt oxide ( $\text{LiCoO}_2$ )

Several oxides with a general formula  $\text{LiMO}_2$  (M=V, Cr, Co and Ni) crystallize in a layered structure in which the  $\text{Li}^+$  and  $\text{M}^{3+}$  ions occupy the alternate (111) planes of the rock salt structure to give a layer sequence of O-Li-O-M-O along the c-axis as shown in figure for  $\text{LiCoO}_2$ . The structure has an oxygen stacking sequence of .....ABCABC..... along the c-axis and the  $\text{Li}^+$  and  $\text{M}^{3+}$  ions occupy the octahedral interstitial sites of the cubic close-packed oxygen array. This structure is designated as the  $\text{O}_3$  layer structure since the  $\text{Li}^+$  ions occupy the octahedral sites (O referring to octahedral) and there are three  $\text{MO}_2$  sheets per unit cell. The structure with a strongly (covalently) bonded  $\text{MO}_2$  layers allows a reversible extraction/insertion of lithium ions from/into the lithium planes. The interconnected lithium ion sites through the edge-shared  $\text{LiO}_6$  octahedral arrangement between the  $\text{MO}_2$  layers provide fast two dimensional lithium-ion diffusion leading to high  $\sigma_{\text{Li}}$ . On the other hand, the edge-shared  $\text{MO}_6$  octahedral arrangement with a direct M-M interaction can provide good electronic conductivity depending on the electronic configuration of the  $\text{M}^{3+}$  ion. As a result, the  $\text{LiMO}_2$  oxides crystallizing in the  $\text{O}_3$  structure have been attractive candidates as cathodes.

The  $\text{LiCoO}_2$  is commonly used in the positive electrode<sup>11,12</sup> of lithium rechargeable batteries, due to its high energy density, high specific capacity, high cycling stability and long shelf life whose operation is based on reversible insertion and removal of lithium ions to and from their positive and negative electrodes.  $\text{LiCoO}_2$  has the  $\alpha\text{-NaFeO}_2$  structure with the oxygen's in a

cubic close-packed arrangement on complete removal of the lithium, the oxygen layers rearrange themselves to give hexagonal close packing of the oxygen in  $\text{CoO}_2$ <sup>13</sup>. Between these composition limits several phases are formed with varying degrees of distortion of the ccp oxygen lattice. The  $\text{LiCoO}_2$  has layered crystalline structure with R3m symmetry in which the cobalt ions reside on the 3a sites of the octahedron, the lithium ions reside on the octahedral 3b interstices and the oxygen anions form cubic close packing as shown in figure-3<sup>14</sup>.

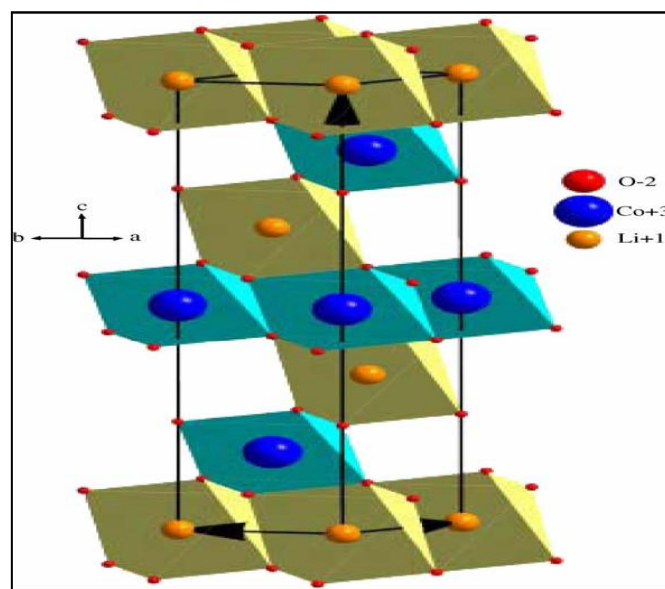


Figure-3  
 Structure of  $\text{LiCoO}_2$

### Conclusions

Today's tendency is to create solid-state integrable microbatteries that are compatible with semiconductor technologies. Such integrated microbattery compatible with the dimensions of micro-devices will act as a source of power for many single components in integrated circuits and devices, which avoids electrical conduction leaks, inevitable power losses, cross talking and allows three dimensional integration. Thin films of functional materials including oxide ceramics have become important for use in many electronic, photonic, magnetic, ionic, etc., devices. Most of them have been fabricated through the so-called highly technical processing routes that require a high consumption of energy. The lithium battery industry is undergoing rapid expansion, now representing the largest segment of the portable battery industry and dominating the computer, cell phone, and camera power source industry. The  $\text{LiCoO}_2$  is commonly used in the positive electrode of lithium rechargeable batteries, due to its high energy density, high specific capacity, high cycling stability and long shelf life whose operation is based on reversible insertion and removal of lithium ions to and from their positive and negative electrodes.

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