General introduction on lithium batteries

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(pos-doc)

Advisor: Prof. Piercarlo Mustarelli
General introduction on lithium batteries

- Battery: definition
- Some historical aspects
- Batteries types
- Lithium batteries
- Research activity in lithium batteries
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2. Some historical aspects
3. Batteries types
4. Lithium batteries
5. Research activity in lithium batteries
Batteries

Definition: devices that transform chemical energy into electricity

Every battery has two terminals: the positive cathode (+) and the negative anode (-)

Functioning

Device switched on  ➔  chemical reaction started  ➔

 electrons produced  ➔  electrons travel from (-) to (+)

➔  electrical work is produced

Source: http://chemistry.hull.ac.uk/lectures/mgf/Lithium-Ion%20Batteries.ppt#256,1,Lithium-Ion Batteries
Electrochemical Cell

Batteries consist of electrochemical cells that are electrically connected. An **electrochemical cell** comprises:

1. a negative electrode to which anions (negatively-charged ions) migrate, i.e. the anode - donates electrons to the external circuit as the cell discharges;

2. a positive electrode to which cations (positively-charged ions) migrate, i.e. the cathode.

3. electrolyte solution containing dissociated salts, which enable ion transfer between the two electrodes, providing a mechanism for charge to flow between positive and negative electrodes;

4. a separator which electrically isolates the positive and negative electrodes.

Source: http://chemistry.hull.ac.uk/lectures/mgf/Lithium-Ion%20Batteries.ppt#256,1, Lithium-Ion Batteries
General introduction on lithium batteries

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Battery History

<table>
<thead>
<tr>
<th>Time</th>
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<td>1800</td>
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<td>Giant battery (2,000 cells)</td>
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<td>Electricity from magnetism</td>
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<td>1992</td>
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<td>1995</td>
<td>Recent developments</td>
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</table>

Battery History

- The modern battery was developed by Alessandro Volta in 1800.
- Ingredients: Zinc, Saltwater paper, and Silver
- An electrochemical reaction.
- The “Voltaic Pile”

Source: http://www.kentlaw.iit.edu/faculty/fbosselman/classes/Spring2008/Pow...
Battery History

- Shortly after Volta Leclanche introduced the zinc–carbon cell;
- 1859: Gaston Plante the lead-acid battery;
- 1899 by Waldemar Jungner with the nickel–cadmium battery.
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Primary vs. Secondary Batteries

✓ Primary batteries are disposable because their electrochemical reaction cannot be reversed.

✓ Secondary batteries are rechargeable, because their electrochemical reaction can be reversed by applying a certain voltage to the battery in the opposite direction of the discharge.

Source: http://www.kentlaw.iit.edu/faculty/fbosselman/classes/Spring2008/PowerPoints/BryanLamble.ppt
Standard Modern Batteries

- **Zinc-Carbon**: used in all inexpensive AA, C and D dry-cell batteries. The electrodes are zinc and carbon, with an acidic paste between them that serves as the electrolyte. (disposable);

- **Alkaline**: used in common Duracell and Energizer batteries, the electrodes are zinc and manganese-oxide, with an alkaline electrolyte. (disposable);

- **Lead-Acid**: used in cars, the electrodes are lead and lead-oxide, with an acidic electrolyte. (rechargeable).
Battery types (cont’d)

- **Nickel-cadmium**: (NiCd)
  - rechargeable,
  - “memory effect”

- **Nickel-metal hydride**: (NiMH)
  - rechargeable
  - “memory effect” (*less susceptible than NiCd*)

- **Lithium-Ion**: (Li-Ion)
  - rechargeable
  - *no “memory effect”*

“High energy density, power rate, cycle life, costly”
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Lithium Battery Development

- Pioneering work for the lithium battery began in 1912 by G. N. Lewis but it was not until the early 1970’s when the first non-rechargeable lithium batteries became commercially available.

- In the 1970’s, Lithium metal was used but its instability rendered it unsafe.
Attempts to develop rechargeable lithium batteries followed in the eighties, but failed due to safety problems.

The Lithium-Ion battery has a slightly lower energy density than Lithium metal, but is much safer. Introduced by Sony in 1991.
1972 Define the concept of chemical intercalation

1972 Define the concept of chemical intercalation

In chemistry, intercalation is the reversible inclusion of a molecule between two other molecules. Ex: graphite intercalation compounds.
Lithium secondary battery

1972 Define the concept of chemical intercalation

In chemistry, intercalation is the process involving the inclusion of a molecule (or group) between two other molecules (or groups). Examples include DNA intercalation and graphite intercalation compounds, etc.

Graphite intercalation compounds are complex materials where an atom, ion, or molecule is inserted (intercalated) between the graphite layers. In this type of compound the graphite layers remain largely intact and the guest species are located in between.

Figure: Space-filling model of potassium graphite KC8 (side view) from: http://en.wikipedia.org/wiki/Graphite_intercalation_compound
A Li-ion battery is an electrochemical device which converts stored chemical energy directly into electricity.

- During charging, an external voltage source pulls electrons from the cathode through an external circuit to the anode and causes Li-ions to move from the cathode to the anode by transport through an liquid electrolyte.
- During discharge, the processes are reversed. Li-ions move from the anode to the cathode through the electrolyte while electrons flow through the external circuit from the anode to the cathode and produce power.

Source: http://www.math.wpi.edu/MP12008/TIAX/MPI-web.ppt#256,1, Modeling battery electrode properties
Principle of Operation

**Charging**

\[ \text{Co}^{3+} \rightarrow \text{Co}^{4+} \]

**Discharging**

\[ \text{Co}^{4+} \rightarrow \text{Co}^{3+} \]

More details on the transport of Li-ions.

- Both the anode and cathode are made from a collection of powder particles which are bonded together into a 3-D porous body (electrode).
- During discharge, ion transport in the electrode occurs as follows (green line)
  1. Li-ion starts in the bulk of a anode particle.
  2. It undergoes solid state diffusion in the particle.
  3. At the surface it disassociates from the e⁻ and enters the electrolyte which occupies the pores of the electrode.
  4. The ion is transported through the electrolyte (liquid phase diffusion) to the cathode.
  5. In enters the cathode.
  6. It undergoes solid state diffusion in the cathode.
- At the same time, the electron must pass through the collection of solid particles to a metal current collector where it can be extracted from the cell and used to power a device (red line). It can not travel in the electrolyte.

Source: http://www.math.wpi.edu/MP12008/TIA08MPI-web.ppt#256,1,Modeling battery electrode properties
Key Battery Attributes

- **Energy Density:** Total amount of energy that can be stored per unit mass or volume. How long will your laptop run before it must be recharged?

- **Power Density:** Maximum rate of energy discharge per unit mass or volume. Low power: laptop, i-pod. High power: power tools.

- **Safety:** At high temperatures, certain battery components will breakdown and can undergo exothermic reactions.

- **Life:** Stability of energy density and power density with repeated cycling is needed for the long life required in many applications.

- **Cost:** Must compete with other energy storage technologies.

Source: http://www.math.wpi.edu/MPIC2008/TIAX/MPIC-web.ppt#256,1,Modeling battery electrode properties
Advantages of Using Li-Ion Batteries

- **POWER** – High energy density means greater power in a smaller package.
  - 160% greater than NiMH
  - 220% greater than NiCd

- **HIGHER VOLTAGE** – a strong current allows it to power complex mechanical devices.

- **LONG SELF-LIFE** – only 5% discharge loss per month.
  - 10% for NiMH, 20% for NiCd

Source: http://www.kentlaw.iit.edu/faculty/fbosselman/classes/Spring2008/PowerPoints/BryanLamble.ppt
Comparison of the different battery technologies in terms of volumetric and gravimetric energy density.

Lithium Battery Evolution

![Graph showing the evolution of lithium battery sales from 1995 to 2011. The graph compares NiCd, NiMH, Li-ion, and Li-polymer batteries. The graph indicates a shift from NiCd and NiMH batteries to Li-ion and Li-polymer batteries over time.]

Cathode Materials Challenges:

- The most desirable cathode materials are strong oxidizing agents that can react with and decompose organic electrolytes;

- In extreme cases, problems with internal shorts or improper voltages can trigger exothermic reactions, leading to thermal runaway and catastrophic failure.

Source: http://ecow.engr.wisc.edu/cgi-bin/getbig/interegr/160/johnmurphy/3lectureno/archivedle/lecture15_walz.ppt#299,1,Energy Storage, Lithium Ion Batteries, and Electric Vehicles
Electrolyte Challenges:

- Liquid electrolyte

  ✓ Problems: leakage, sealing, non-flexibility of the cells, side reactions with charged electrodes;

  ▼ Explosions

Outcome Of Catastrophic Battery Failure

Source: http://www.ostp.gov/galleries/PCAST/zinc_matrix.ppt#295,1,Advanced Battery Technology
Dell Recalls Notebook Batteries

SAN FRANCISCO/TOKYO (Reuters) - Dell Inc. (DELL.O) said on Monday it will recall 4.1 million notebook computer batteries because they could overheat and catch fire, in the biggest recall in its 22-year history.

May 29, 2006
8:28 am US/central
By David Schechter

(WCCO) Nick Brown, 11, was playing on his Apple iBook laptop about one month ago when, like most children, he got distracted and left the room.

His mom, Cindy Brown, explains what happened next. "My husband and I were in the other room, heard a popping noise, came out and the room was filled with smoke," she said.

HP issues battery fire hazard recall number 3

Hewlett-Packard, appears to have a serious quality control problem with its battery powered systems. The giant computer maker has just issued its third major global product recall because of potential fire hazards to consumers within just nine months.

In its latest recall, the largest to date, HP has issued a public recall notice for 679,000 model R707 digital cameras sold between August 2004 and April 2006.

Source: http://ecow.engr.wisc.edu/cgi-bin/getbig/interegr/160/johnmurphy/3lectureno/archivedle/lecture15_walz.ppt#299,1,Energy Storage, Lithium Ion Batteries, and Electric Vehicles
None of the existing electrode materials alone can deliver all the required performance characteristics including high capacity, higher operating voltage, long cycle life and safety.

RESEARCH AND DEVELOPMENT

Source: modified from http://www.kentlaw.iit.edu/faculty/fbosselman/classes/Spring2008/PowerPoints/BryanLamble.ppt
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Active materials for rechargeable Li-based cells

LiFePO$_4$ active material for lithium batteries

- Potentially low cost and plentiful elements;
- Environmentally benign;
- Theoretical capacity = 170 mAh/g
- Different synthetic methods: sol-gel, solid state, hydrothermal...


Structures of orthorhombic LiFePO$_4$ and trigonal quartz-like FePO$_4$. 

34
Influence of the synthesis temperature and purity

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sintering temperature (°C)</th>
<th>The lattice parameters</th>
<th>Crystallite size $D_{131}$ (nm)</th>
<th>Particle size (nm)</th>
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<tbody>
<tr>
<td>LiFePO$_4$</td>
<td>500 (a)</td>
<td>1.032 0.5996 0.4689</td>
<td>38</td>
<td>90–230</td>
</tr>
<tr>
<td></td>
<td>600 (b)</td>
<td>1.031 0.5998 0.4687</td>
<td>49</td>
<td>120–350</td>
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<tr>
<td></td>
<td>700 (c)</td>
<td>1.031 0.6001 0.4686</td>
<td>75</td>
<td>150–800</td>
</tr>
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</table>

Fig. 4. TEM photograph of samples synthesized at different temperature: (a) 600 °C; (b) 700 °C.

Influence of the carbon coating

Fig. 8. TEM observation of LiFePO$_4$/C composite prepared by MA method.

Fig. 3. Initial charge and discharge capacities of LiFePO$_4$ and LiFePO$_4$/C samples prepared at different temperatures (a) 500 °C, (b) 600 °C and (c) 700 °C at C/5 rate.

Influence of the amount of carbon

Fig. 1. Photographs of LiFePO₄ powders containing varying amounts of in situ carbon. The first three samples were prepared by sol–gel synthesis following procedures outlined in Ref. [11], and the rightmost sample was prepared by the solid-state reaction described by Yamada et al. [21].

Fig. 5. Cycling performance at 1C rate for LiFePO$_4$/MCMB batteries. LiFePO$_4$/C composites as cathode materials are synthesized with: (a) 0 wt.%; (b) 1.7 wt.%; (c) 3.4 wt.%; (d) 5.1 wt.%; (e) 6.8 wt.%; (f) 8.5 wt.% glucose, respectively.

Influence of the type of carbon


Figure 2. Electrochemical discharge capacity of LiFePO₄ electrodes in lithium cells v.s. structure of residual carbon. Decreasing D/G and sp²/sp³ band ratios indicate increased amounts of graphene clusters in the structure.

Influence of the cathode thickness

**Figure 2.** Discharge curves of LiFePO$_4$ electrodes with different thicknesses at a rate of 2 C in 1 M LiPF$_6$ EC/DEC = 3:7 by volume.

Cathode Composition (weight%)
- 70-80% LiFePO$_4$
- 10-20% Carbon (carbon black or graphite)
- 5-10% PVDF

Electrolytes

- Li salt dissolved in a solvent.

- LIB Operation range: 3.0-4.2 V,
  Decomposition potential of H₂O = 1.23 V
  Aqueous electrolyte not used

## Electrolytes

Italian groups involved in lithium ion battery R&D

<table>
<thead>
<tr>
<th>Institution</th>
<th>Topic</th>
<th>Sponsor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Department of Chemistry, University of Rome “La Sapienza”</td>
<td>New cathodes materials: LiNi$<em>x$Co$</em>{1-x}$O$_2$; iron phosphates; new anode materials: lithium alloys, inter-metallic compounds. Lithium polymer electrolytes; composite lithium conducting membranes</td>
<td>MIUR$^a$, CNR$^b$</td>
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<tr>
<td>Faculty of Pharmacy, University of Bologna Department of Chemistry, University of Camerino</td>
<td>Manganese spinel cathode materials. Active carbon anodes Large surface area carbon anodes; lithium-rich graphites</td>
<td>MIUR$^a$, CNR$^b$, CNR$^b$</td>
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<tr>
<td>Department of Chemistry, University of Pavia</td>
<td>Lithium polymer electrolytes</td>
<td>MIUR$^a$, CNR$^b$</td>
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<tr>
<td>Department of Materials Science &amp; Chemical Eng Polytechnic of Turin Faculty of Pharmacy, University of Chieti Center for Electrochemistry of Interfaces, Rome ENEA, Casaccia, Rome</td>
<td>New cathodes materials: substituted iron phosphates Iron phosphate cathodes; nano-composite polymer electrolytes. Substituted manganese spinel cathodes Iron phosphate cathodes; polymer electrolytes; fabrication and test of lithium ion battery prototypes</td>
<td>MIUR$^a$, CNR$^b$, CNR$^b$, MIUR$^a$</td>
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</tbody>
</table>

$^a$ Italian Ministry for University and Research.  
$^b$ Italian National Research Council.


- **4 types of non-aqueous electrolytes in use:** organic liquid, gel, polymer and ceramic-solid electrolytes.

A salt (LiPF$_6$, LiClO$_4$, etc.) dissolved in a high-molecular-weight polymer matrix (should contain a heteroatom): Poly(ethylene oxide) PEO

Chemically stable – contains only C-O, C-C and C-H bonds.

Cation mobility - cation-ether-oxygen co-ordination bonds, regulation - local relaxation and segmental motion of the PEO polymer chains -> ionic conductivity of the electrolyte.

Solid polymer electrolytes: advantages to liquid electrolytes

- High reversibility of the processes (high electrochemical stability);
- Solid => no risk of leakage of electrolyte;
- Can be used in a wider range of temperature;
- Lightweight
- High Flexibility
- Possibility of miniaturization.
Problems: low conductivities at or below room temperature (10^-8 to 10^-5 S/cm)

1) Preparation of crosslinked polymer networks, random, block or comb-like copolymers, with short chains of ethylene oxide, in order to minimize crystallization;

2) Utilization of doping salts which form low temperature eutectics with pristine PEO phase (plasticizing salts): ex: LiN(CF$_3$SO$_2$)$_n$(n = 2–5);

3) Utilization of organic plasticizers to increase the flexibility of the host polymer chains;

4) The addition of inorganic and/or organic additives, with the aim of reducing the crystallizing ability of the polyether host without reducing the mechanical properties of the system.

More recently: gel electrolytes: polymer matrix are solvated by a large amount of the trapped solvent;

- Polymer acts like a support;
- high value of conductivity at room temperature ($10^{-2}$–$10^{-4}$ S/cm),
- ionic liquid $\rightarrow$ research activity.

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Fig. 1. Picture of PVDF gel electrolyte.

LIB Technology

Different configurations:  
a) cylindrical  b) coin  c) prismatic  d) thin and flat (pLiON).

Thank you for your attention!!