

LITHIUM-METAL-POLYMER BATTERIES: FROM THE ELECTROCHEMICAL CELL TO THE INTEGRATED ENERGY STORAGE SYSTEM

Violaine Dorval
Market Development Manager

Christian St-Pierre
Marketing Director

Alain Vallée
Vice-President, Technology

AVESTOR
Boucherville, Quebec, CANADA

INTRODUCTION

AVESTOR's lithium-metal-polymer technology is an advanced battery system for stationary and automotive applications. Papers have been presented at Battcon in past years on this technology^{1,2}, focusing on basics of the electrochemistry, key benefits in application and field test results. The present paper will describe the electrochemical system in more detail and define the subsystems that optimize the operation of the battery.

The lithium-metal-polymer battery utilizes a simple electrochemical configuration composed of a metallic lithium anode, a simple copolymer based on polyether chemistry, vanadium oxide and a lithium salt, lithium bistrifluoromethanesulfonamide (LiTFSI). What are the specifics of the LMP electrochemistry and how does it impact the properties and performance of the battery? What makes this technology so unique? This paper will answer these questions by describing and explaining the electrochemistry and the resulting properties of the electrochemical cell.

To optimize the battery performance, certain conditions are required and are achieved by control subsystems, integrated into the battery construction. This paper will define and explain these main subsystems, their function and their influence on the operation and performance. The subsystems that will be discussed are:

- Thermal management - to maintain cell temperature at 40°C minimum during float and at 60°C minimum during discharge and recharge
- Pressure Subsystem - to ensure the stability of the interface between the anode and the electrolyte
- Cell equalisation - cell balancing to maintain all cells at a uniform floating voltage and cell topping to regularly condition each cell to 3.1 V after each deep discharge
- Charge control - to prevent excessive charge current or overvoltage
- Disconnect Switching - to protect the battery against operation under excessive, abnormal conditions

Finally, this paper will summarize how the electrochemistry and its integrated subsystems impact the entire system application and its operation from an end-user perspective.

THE LMP ELECTROCHEMICAL MECHANISM

Any battery technology is composed of a grouping of electrochemical cells interconnected in a combination of series and/or parallel configurations to provide the desired voltage and capacity. Each cell, in turn, is composed of a positive electrode, the cathode, and a negative electrode, the anode, physically separated by an electrolyte containing dissociated salt that provides the medium for ionic transfer between the two electrodes. When the electrodes are connected together by an external, electrically conductive circuit, the battery's chemical reaction is activated at both electrodes, liberating and transporting electrons from one electrode to the other. The cells convert their chemical energy into electric energy. The most advantageous combinations of anode and cathode materials are those that provide the most efficient and complete conversion of their chemical energy and have the highest cell voltage and energy storage capacity for unit weight and volume.

The quest for a stationary battery technology that could use metallic lithium as its anode was driven by the fact that the lithium is the lightest and the most electropositive of metals (3.04 Volts, against the hydrogen reference electrode). The specific energy of lithium metal, at 3800 Ah/kg (1727 Ah/lb), compares very favourably against materials traditionally used in stationary batteries, such as lead, at 260 Ah/kg (118 Ah/lb), and cadmium, at 480 Ah/kg (218 Ah/lb). Figure 1 indicates the comparative positioning of available battery technologies with respect to their energy densities.

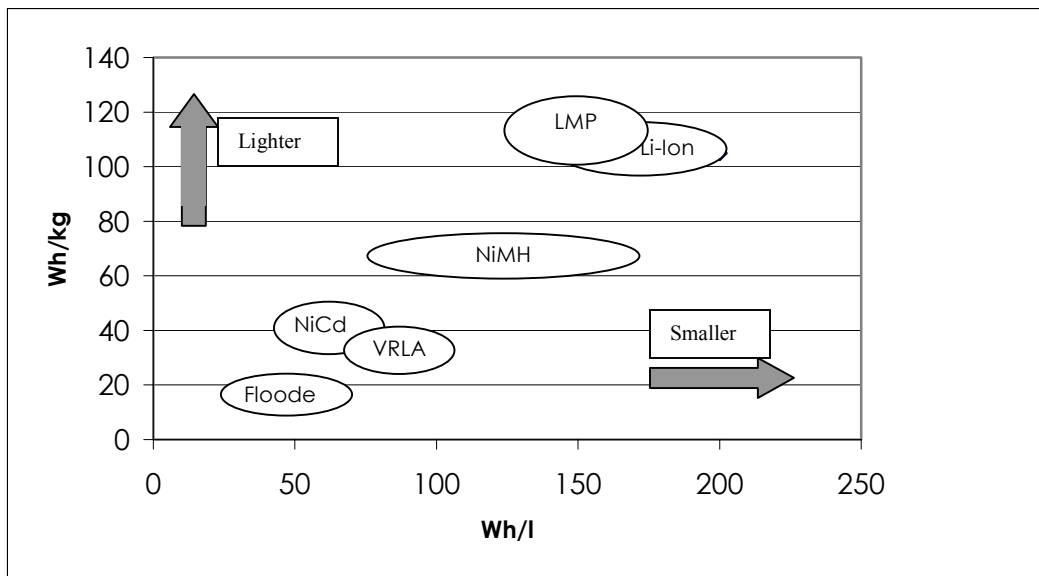


Figure 1: Specific Energy and Energy Density – Technology Comparison

For the unique lithium-metal-polymer battery technology, the electrochemical cell is composed only of materials in their solid state - two electrodes physically separated by a dry solid polymer as illustrated in Figure 2.

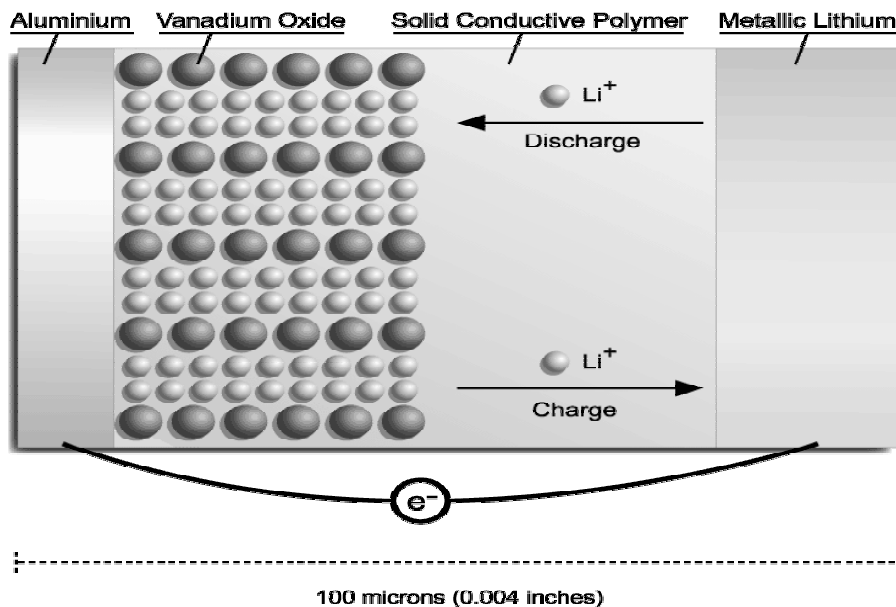


Figure 2: LMP Technology Electrochemical System

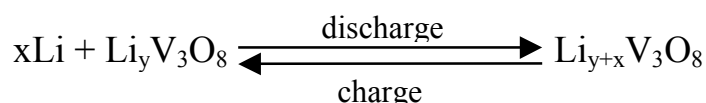
The anode is an ultra-thin metallic lithium foil that services as a lithium ion source and a current collector.

The cathode is a composite electrode based on a blend of a reversible intercalation compound of vanadium oxide, carbon black, lithium salt and polymer laminated to a thin aluminium foil that serves as a collector.

The unique aspect of the LMP technology is **the electrolyte**, a solid, dry lithium-ion conducting membrane that also serves as a separator between the anode and cathode foils. It is a solid, rubber type polymer matrix with an ionic lithium salt complexed into the matrix. The elastic behaviour of the polymer assures a perfect interface to the surfaces of the two electrodes.

The phenomenon of complexation of polyethers with alkaline salt has been known since 1966 when Moacanin and Cuddihy³ published a thermo-mechanical study demonstrating the solubility of lithium perchlorate (LiClO₄) in polyoxypropylene. The solubility of the salt in the polymer was explained to be the result of an electrostatic interaction between the cation of the salt and the free electrons doublets of the oxygen atom in the polyether. The conductivity property of this type of complex was demonstrated for the first time by Wright⁴ in 1975. In 1979, Armand, *et al.*,⁵ proposed the concept of using a polyether-salt complex, as a thin film electrolyte in a rechargeable lithium battery, demonstrating that the ionic conductivity, ion motion, was the result of the displacement of the ionic species in the amorphous portion of the electrolyte and giving birth to the LMP technology.

The result is a totally solid state electrochemical cell, having neither liquid nor gel component, in which near 100 % of the mass is made of electrochemically active materials. The cell reaction is an intercalation of lithium ions into the structure of the vanadium oxide of the cathode during the discharge cycle and a deintercalation of lithium ions from the charged cathode and its redeposition onto the anode during charge:



Ionic Conductivity

The ionic conductivity in the lithium-based polymer electrolyte is also related to the fundamental concept of ion dissociation and transport. The best performance in terms of ionic conductivity in a polyether matrix has been achieved with lithium perfluorosulphonimide (Li(CF₃SO₂NSO₂CF₃)) salt (LiTFSI) due to the extensive charge delocalisation of its anion. In pure polyethylene oxide (PEO), LiTFSI demonstrates an order of magnitude improvement over common lithium trifluoromethane sulfonate salt (LiCF₃SO₃).

The LMP technology is based on a polyether copolymer matrix in which the LiTFSI salt is dissolved. Polyethylene oxide has a tendency to be highly crystalline. The introduction of a comonomer reduces the crystallinity of the polymer and improves its ionic conductivity below 60°C (140°F) (Figure 3). However, even this combination of low crystallinity polyether and lithium salt cannot provide the required conductivity of at least 1 x10⁻⁴ Siemens/cm (2.54 x10⁻¹⁰ S/inch) below 40°C (104°F). The stability of the combination's ionic conductivity at high temperatures, however, produces one of the major advantages of the LMP system, excellent long-term performance in high temperature environments.

The Thermal Management Subsystem

To compensate for the loss of ionic conductivity at temperatures below 40°C (104°F), the LMP battery is designed with an integrated, autonomous thermal management system. An electronic control system and heating element layers interspersed through the electrochemical cell stack equip the battery to control its own internal temperature. During float and short discharges, the battery's thermal management system maintains its internal temperature at 40°C (104°F). For longer discharges, the system increases internal temperature to 60°C (140°F). In application by the end-user, this results in a battery that can operate in an uncontrolled environment over a temperature range of -40°C to 65°C (-40°F to 149°F), without any external heating or cooling devices.

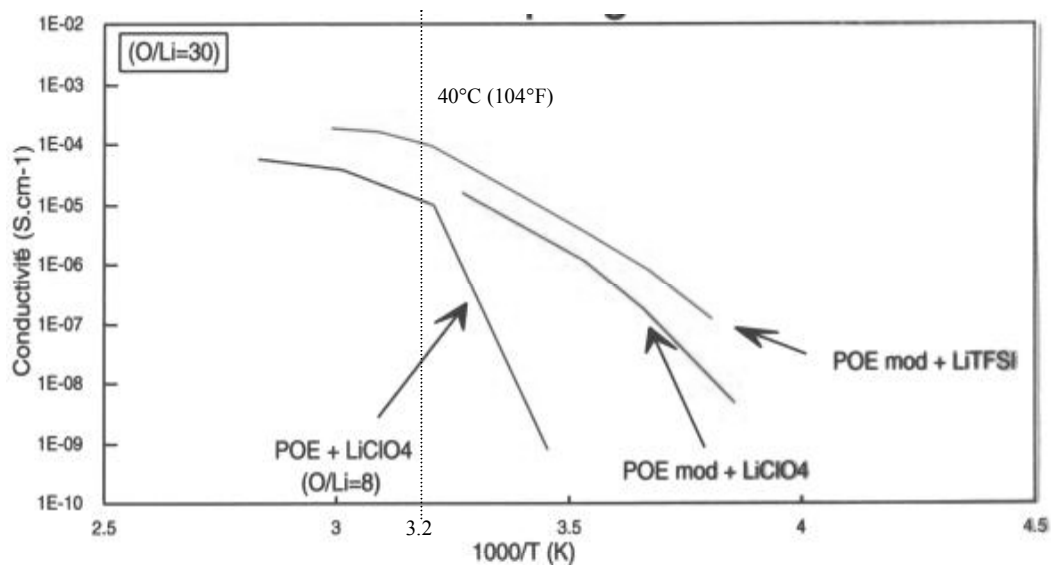


Figure 3: Arrhenius Plot of Conductivity for Selected Polymer Electrolytes

CYCLING PERFORMANCE

The mechanical properties and chemical composition of the polymer electrolyte play an important role in the performance and safety of the electrochemical cell over its charge/discharge cycling life. The polymer electrolyte serves as a separator, insulating the electrodes from each other. A known phenomenon common to all alkali metal-based electrochemical cell technologies is an important morphological evolution of the metallic anode, lithium in this case, to form dendrites when recharged in the presence of organic electrolytes. This can lead to short circuits between the electrodes. The mechanism of this phenomenon may be explained as follows:

1. The lithium is thermodynamically unstable in the presence of the organic electrolyte (solvent + lithium salt) and produces an oxidation layer, which is more or less passivating and, under certain conditions, remains a conductor for lithium ions. (A conductive, passivating oxidation layer is referred to as a solid electrolyte interface (SEI));
2. During consecutive cycles of charge and discharge, lithium is dissolved and is re-deposited unevenly and, progressively, becomes electrically insulated or is chemically consumed by reaction with the organic electrolyte;
3. The result is the formation of a porous and irregular anode consisting of dispersed lithium that is partially passivated. This causes a consequent loss of capacity for the anode.

It has been observed that this phenomenon of formation of lithium dendrite may also take place in the presence of a polymer electrolyte albeit to a lesser degree than that in the presence of liquid electrolytes. This has been confirmed with a lithium anode cycled under repetitive conditions by Bélanger, *et al*⁶.

In the LMP technology, the lithium anode consists of a thin metallic sheet, less than 50 micrometers (0.002 inch) thick, which includes at its surface a solid electrolyte interface (SEI) passivation film, conductive to alkali metal ions. This film acts to limit the reaction between the lithium and the polymer electrolyte and to support the exchange of lithium ions during charge/discharge cycles. Furthermore, the polymer electrolyte design is resistant to mechanical deformation and can, thus, transmit pressure on to the surface of the lithium anode to resist the metal's dendritic stress.

The Pressure Subsystem & Charging Current Limiter

To take advantage of these characteristics, the LMP battery is constructed with a pressure system (see Figure 4) to maintain pressure over the stacked electrochemical cells, assuring the uniformity of the lithium plating process that occurs during charging, preserving the integrity of the lithium-polymer electrolyte interface during consecutive cycles of dissolution/plating and containing the dendritic stress. This assures the high coulombic efficiency of the LMP cell over its cycle life.

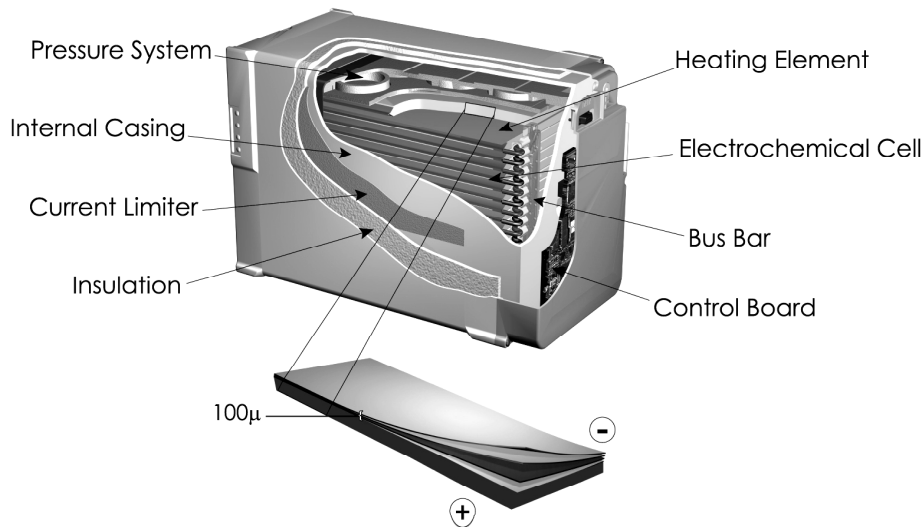


Figure 4: LMP Cell and Battery Construction

The mechanical pressure system can only maintain the uniformity of the lithium foil surface if the rate of plating is slow. Consequently, the charging current must be limited to a maximum of $C/8$ to prevent battery deterioration over its life. The LMP battery is equipped with a current limiter system to maintain the charging current within an acceptable range even if the battery is connected to a high capacity charger. The current limiter system switches resistance connected in series with the charging circuit to control the charging current as a function of the battery voltage.

CHARGE/DISCHARGE MECHANISM

Cell Equalization Subsystem

In the LMP electrochemical cell, there is no secondary reaction comparable to electrolysis in liquid electrolyte systems during the recharge to limit the voltage at the end of charge. The electrochemical leakage current, although very small, is not equal from one cell to another. Over time, this difference can gradually unbalance the cells, causing those cells with higher leakage current to have a lower voltage. During a discharge, the low voltage cells would result in a reduction of the delivered energy capacity. To correct this effect, a cell balancing subsystem is integrated into the battery to equalize the cells. The LMP battery maintains its internal cell imbalance within a range of 40-100 mV. The equalization system performs its function by exercising an internal switching matrix that discharges the high voltage cells through a small resistance to recharge the low voltage cells. The equalization is performed at a voltage above the nominal battery voltage, e.g., above 49.5V on a 48V battery. The balancing system assures long battery life, eliminates the need to match the cells according to capacity during assembly and eliminates the need for any cell balancing procedure external to the battery module.

As explained earlier, during discharge lithium ions intercalate into the vanadium oxide. After a deep discharge the structure of the vanadium oxide can change, trapping ions in the oxide structure and preventing their return to the anode during the recharge cycle, with a resulting drop in battery capacity. This phenomenon can be reversed by assuring adequate charging at each individual cell level. The LMP battery is equipped with a cell topping system. After each deep discharge, the voltage of each cell, one by one, is brought back to 3.1 volts, allowing the vanadium oxide to return to its initial state. This system makes use of the same switching matrix as the cell balancing system. Following the cell topping process, cell voltages are maintained within the normal floating range of 3.0 to 3.1V.

The Voltage Profile, the Charge Control Subsystem and the Disconnect Switch

The reversible voltage range of the LMP electrochemical cell is 2.0 to 3.1 V. If the cell is operated outside this range it will lose capacity rapidly. To assure the battery's long service life, it is equipped with a control subsystem that will open the charging circuit in case of overcharge or open the discharge circuit under over-discharge, short circuit or reverse polarity conditions.

A typical voltage profile showing the relation between the voltage curve of the AVESTOR 48 volt battery (model SE48S63) and the charge control subsystem trigger points is shown in Figure 5. This battery is maintained at a float voltage in the range of 53.8 to 55.8V. During the discharge cycle, the battery voltages follows a relatively linear decline over the entire usable capacity, reaching 42V after delivering 100% of its rated capacity. At 41V the battery's internal heaters are deactivated, and at 39.5V, the automatic disconnect removes the battery from the circuit. The battery will automatically reconnect for recharge on presence of a charging source. An emergency disconnect will activate at 30.6V (1.7V/cell) if the battery should reach approximately 35% overdischarge and will necessitate the return of the battery to the factory for appropriate reset and verification procedures prior to being returned into service.

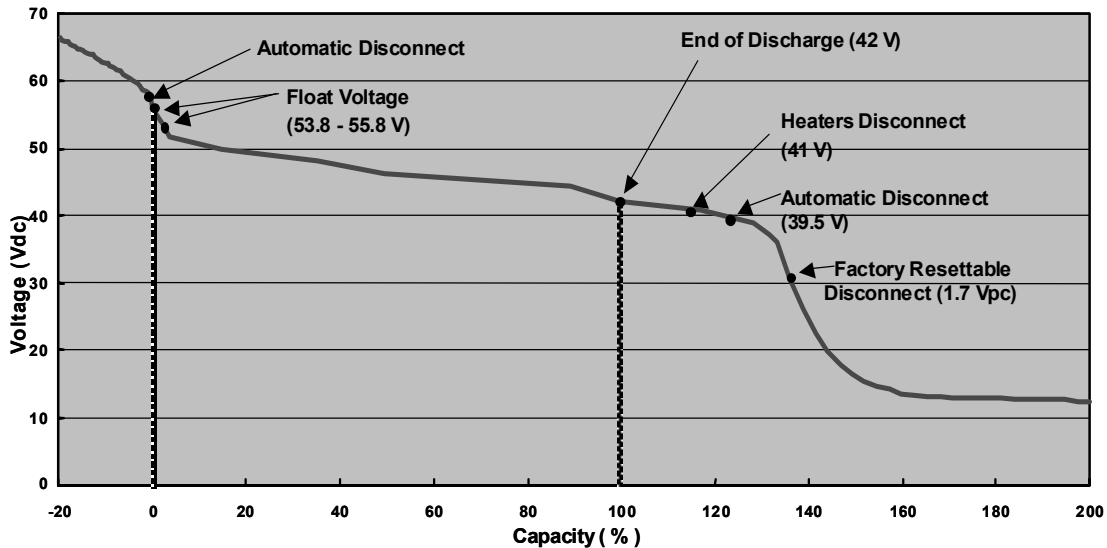


Figure 5: Typical Battery Voltage Profile vs. Charge Level

THE INTEGRATED BATTERY INTELLIGENCE SYSTEM

The benign, solid state environment internal to an LMP battery and its functional requirements for certain electronic internal control subsystems as discussed above leads logically to the integration of electronic "smarts" into each LMP battery module. The module controller continuously monitors:

- cell voltages
- battery voltage
- battery current
- module internal temperatures
- module operating status

and manages the battery operating conditions to optimize the battery's performance and life by:

- optimizing cell temperature according to load requirements
- minimizing energy utilized for internal control
- providing charge current limits
- managing internal cell equalization
- providing short circuit and over temperature cut-off protection
- providing overcharge and overdischarge cut-off

The implementation of this functionality internal to the battery renders measurement and control more direct and effective than could be imagined in any other existing electrochemical system and contributes to the stable and dependable characteristics and high ambient temperature tolerance of the lithium-metal-polymer battery module. The controller provided for this purposes is also available to provide data on battery operation and internal monitoring of information relevant to state of health and state of charge determination. This information can be accessed at various levels of detail, by simple go/no go indicators on each battery case, by on site connection to data terminals on the battery or through a remote data monitoring system, according to the strategy and needs of the energy storage system end-user.

CONCLUSION – A ROBUST AND VERSATILE BATTERY DESIGN

Over 20 years of research and development in lithium-metal-polymer batteries has resulted in a revolutionary design for stationary batteries offering high energy density, reliability and long life under the most extreme environmental conditions.

The AVESTOR LMP battery is now well into the commercialization phase of its first telecommunication product, the SE48S63. This commercial product has now been installed by several major telecommunication companies in a variety of applications including outside cabinets, trailers, huts, and data centers.

The LMP technology offers numerous advantages for the telecom industry, and for all stationary applications :

- complete absence of any liquid component in the lithium-metal-polymer battery
 - elimination of typical liquid level verification and filling procedures
 - elimination of spill containment accessories
 - no risk of freezing or case cracking under exposure to extreme cold temperatures
- all-copper connection terminals that eliminate terminal cleaning and re-torquing procedures
- no gases or other secondary products produced by the primary metal plating reaction internal to the lithium-metal-polymer cell
 - no need for any venting or ventilation equipment
- a stable and predictable aging process.
 - very slow rate of capacity loss, compared to other technologies
 - simplified state of charge and state of health algorithms
- no requirement for external heating or cooling
 - can be installed in unheated and non-air conditioned rooms.
- lower weight and volume of the lithium-metal-polymer battery for equivalent capacities
 - less floor space
 - avoid requirements to reinforce floor structures to support battery system weight.
- elimination of series connections of batteries to achieve desired output voltages
 - increased flexibility in module placement
 - reduced number of cables and connections
 - simplified growth by adding new batteries in parallel with existing units as a function of load

The unique properties of the Lithium-Metal-Polymer electrochemical cell and the features of the subsystems that have been designed into the integrated battery system combine to change the paradigm for users of energy storage systems. The LMP battery system provides unmatched opportunity to simplify the application and management of battery plants and reduce their total life cycle cost.

¹ C. St-Pierre, *et al*, “AVESTOR Lithium-Metal-Polymer Batteries: Proven reliability Based on Customer Trials”, Battcon 2003

² R. Paradis and M. Davis, “The Lithium-Metal-Polymer Energy pack for Stationary Applications”, Battcon 2002

³ J. Moacanin and E.F. Cuddihy, *Journal of Polymer Science, Part C*, Vol.14, p.313, 1966

⁴ P.V. Wright, *British Polymer Journal*, Vol.7, p.319, 1975

⁵ M.B Armand, J.M Chabagno and M.J. Duclot, in Fast Ion Transport in Solids, P. Vashishta, J.N. Mundy and G.K. Shenoy, editors, Elsevier, North Holland, NY, p.131, 1979

⁶ Bélanger, *et al*, Second International Symposium of Polymer Electronics, Siena, Italy, June, 1989