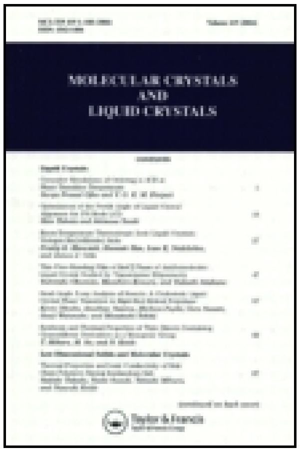

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Polymeric Materials in Energy Storage and Conversion

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Polymeric Materials in Energy Storage and Conversion

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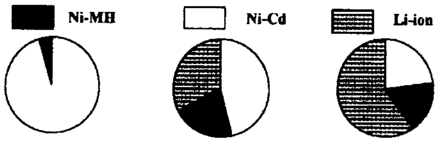
Performances of new batteries and PEM Fuel Cells are tightly dependent on the organic materials, including solvents and plasticizers, salts, polymers and polyelectrolytes. The functional materials must provide high performance but their cost in the event of mass-production is also a key parameter. The paper deals with the organic materials involved in lithium batteries and PEMFC.

<u>Keywords</u>: polymer electrolyte, lithium battery, fuel cell, separator.

INTRODUCTION

The growth rate of the market in portable electronic is mainly related to the demand in camcorders, computers, portable tools and above all cellular phones. The production in rechargeable and portable batteries parallels the growth in electronic. Besides an increase in mass-production, the portable electronic requires an improvement of the battery performances mainly in energy and power densities as well as in specific energy and lifetime. We may distinguish between alcaline batteries, i.e Nickel Cadmium & Nickel Metal Hydride, and lithium batteries. Below, the market shares evolution between 1992 and 1996 which shows the emergence of Nickel -Metal Hydride and lithium-ion batteries, while the market estimates for the end of the century show a prevalent position of lithium-ion batteries.



200 million batteries may be a rough estimate of lithium-ion worldwide production in 1997.

Now, due to environmental issues, several national programms aim to develop electrical cars. Indeed even a partial replacement of thermal vehicles by a significant fleet of electrical cars should reduce the urban pollution acuteness. Safety, lifetime and cost are indisputably the main requirements of the energy sources of an electrical car. At present two batteries are commercially available, i.e lead-acid and Nickel-Cadmium batteries. The specific energy of the former (30 -35 wh/kg) is too low while that of the latter (45-50 wh/kg) may be suitable to western europ cities but unsuited to US cities. As for Nickel Metal Hydride batteries, their specific energy is close to 70 wh/Kg. They appear therefore, despite a high self-discharge rate above 30°C, as a good half-way stage, awaiting high-performance electrical power-supply. For the electrical vehicle -EV- application, both lithium polymer and lithium-ion batteries should compete with Proton Exchange Membrane Fuel Cell (PEMFC). The latter provides an increased autonomy as compared to batteries and, above all, the refilling in fuel should be markedly lower than the time required to recharge the batteries. In addition most of the car manufacturers seem to prefer this solution to batteries, as evidenced by the joint-ventures between Ballard Power Systems and Daimler-Benz or Ford as well as by the demonstration of Toyota and Mercedes prototypes. Nevertheless some problems such as the price, the safety and the size of the fuel cells have to be solved, prior to a mass-production. An industrial scale-up of both batteries and PEMFC for EV application would result in a mass-production of several chemicals. In particular, organic materials i.e salts, polymers and organic solvents are required in lithium batteries, while PEMFC require polyelectrolytes. This paper deals with a description of these organic materials in both batteries and PEMFC.

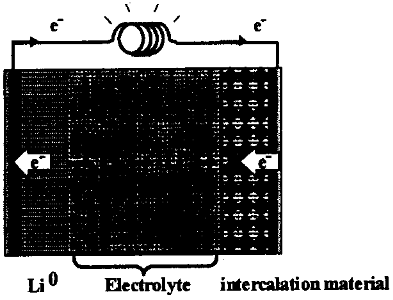
FROM SEPARATORS TO POLYMER ELECTROLYTES IN LITHIUM BATTERIES

As the ohmic resistance of any kind of battery is mainly related to the electrolyte, the battery manufacturers have longstanding tried to decrease the electrolyte thickness. Obviously this thinning down implies the use of a separator in order to avoid a short-circuit of the battery. In this concept the separator is a non-conducting polymer with micropores allowing the liquid electrolytes to circulate between the two electrodes. According to the type of batteries the separator may consist in cellulosic polymer, in polyvinylchloride or in polyolefines such as polyethylene or (and) polypropylene. For instance most of the separators used in alkaline batteries consist in microporous polyamides.

Lithium Batteries Comparison

Batteries with lithium negative electrode

The batteries consist in metallic lithium as a negative electrode and an intercalation material based on a metal sulfide (TiS_2 or MoS_2) or a metal oxide (VO_x, MnO_2) as positve electrode. The main advantage of lithium batteries is related to the very high capacity of metallic lithium # 3.7 Ah/g and to the redox potential Li/Li^+ at -3 volts versus Normal Electrode Hydrogen. Below a lithium polymer battery :



At the laboratory scale these batteries may consist in a liquid electrolyte + separator or a polymer swollen by a liquid electrolyte (salt + organic polar aprotic solvents). Non-rechargeable lithium-metal batteries are produced at large scale and provide high specific energy and low self-discharge rate. But, due in particular to dendrite formation, the cycle life of rechargeable lithium batteries based on liquid electrolyte is limited. Moreover a wide excess of metallic lithium is needed and reduce notably the specific energy of the battery. Now the portable electronic specifications require high conductivities at low temperature (- 20°C) which are only reached with organic liquid electrolytes. To the best of our knowledge, due to safety issues, no any manufacturer, excepted Tadiran Cie, produce these rechargeable batteries. Only lithium polymer batteries, without any addition of liquid solvents, seem to provide both good performances and safety. But their operating temperature ranges between 50 and 80°C, far from the specifications of portable electronic.

Lithium-ion Batteries

In lithium-ion batteries, the negative material consists in a graphite intercalated material. As compared to the previous battery the negative electrode consists in lithium intercalated in a graphite-type material and metallic lithium should be avoided. The replacement of metallic lithium by LiC_6 avoids dendrite formation, improves the safety and allows liquid electrolytes to be used. On the other hand, the specific capacity of the negative electrode # 0.38 Ah/g is obviously decreased as compared to metallic lithium. Nevertheless, due to a wide excess of metallic lithium (5 to 7) in lithium batteries (with liquid electrolytes) the gap between the two negative electrodes is in fact rather limited. In lithium-ion batteries, the positive material, namely $LiCoO_2$, $LiNiO_2$ or $LiMn_2O_4$ is generally at a higher oxidation potential than that used in the previous batteries.

Polymeric Materials for Lithium Batteries

Owing to safety issues and specifications of the applications, polymeric electrolytes without solvents and plasticizers are mainly used with metallic lithium while liquid electrolytes (+ separator) and plasticized polymer electrolytes are mainly used in lithium-ion batteries.

Separator + liquid electrolytes

As compared to aqueous alkaline electrolytes, the conductivities of lithium salts dissolved in aprotic polar solvents are clearly lower. The lithium salt must fulfil several requirements :

- a high solubility ^{3} 1 M in aprotic solvents

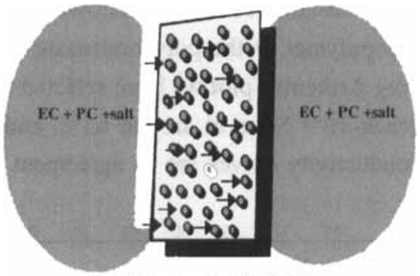
- a high dissociation, which implies a very low nucleophilicity of the anion. Generally it must be a salt of a very strong acid or superacid eg. $LiBF_4$, $LiCF_3SO_3$, $LiAsF_6$ or $LiPF_6$

- a wide electrochemical stability window

- a low to moderate cost

The solvent is in fact a mixture of several aprotic solvents. Most of them, such as ethylene carbonate EC, propylene carbonate PC or gamma butyrolactone GBL have a high dielectric constant. Nevertheless other solvents are sometimes added to PC/EC mixtures in particular ethers (DME) to increase the solvating ability vs Li^+ or linear carbonates to decrease the electrolyte viscosity.

The separator is often a microporous polyolefine such as polyethylene or (and) polypropylene. As the polarity of the polymer is very far from that of the solvents and therefore from that of the liquid electrolyte the micropore wetting is not very good and the incorporation of the separator results in a clear increase of the electrolyte resistance [1]. Below a scheme of a microporous separator:



Microporous polyethylene
Interest : shutdown

The use of low density polyethylene as separators may improve the battery safety. Indeed a short-circuit event results in an clear increase of the temperature. When the latter reaches the melting point of this polyethylene (#110°C) its microporosity vanishes and it behaves as an insulator. This type of device is called shut-down.

Polymer electrolytes

Polymer electrolyte denotes a solution of a salt dissolved in a polymer without addition of any liquid. These "solid" solutions are known since 1964 and their ionic conductivity was first evidenced by P.V.Wright et al. [2] They are well-adapted to batteries for EV application [3]. The polymer electrolyte insures a double function (i) of a separator (ii) of a viscous solvent. The high Donor Number of the oxyethylene repeat unit allows the lithium cation to be solvated by the macromolecular chains. In these electrolytes the ionic conductivity is mainly controlled by the segmental mobility of the polymer chains. Linear high molecular weight poly(oxyethylene) POE has two main drawbacks i.e, a high crystallinity content with a melting point close to 65°C and a creeping tendancy of the polymer electrolytes around 60 - 70°C. The crystallinity results, below the melting point of the polymer electrolyte, in very poor conducting material. By tailoring new polyethers we succeeded in reaching high conductivities in a wide temperature range and notably at ambient temperature. The syntheses should enable an industrial scale-up and provide amorphous networks allowing the polymer electrolytes to be shaped in thin films. For instance unsaturated polyethers were obtained either by a condensation route [4] using a Williamson type synthesis or by anionic polymerization [5] which provides random copolyethers.

In both polyethers the unsaturated moiety allows the crystallinity to be strongly cut and the copolymer or the polycondensate to be hereafter cross-linked. In the following Arrhenius plot we have selected the more conducting electrolytes which reach 10^{-3} S/cm at around 65°C and 10^{-4} S/cm around 30°C (Fig.1). The conductivity curves are in agreement with an usual free-volume behaviour.

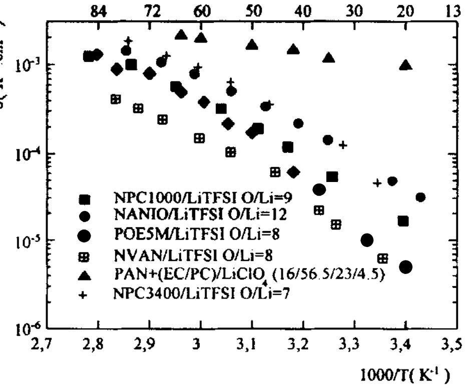


FIGURE 1. Comparaison of the best conductivity levels for several complexes

NPC 1000 and NPC 3400 means cross-linked polycondensate in which the solvating polyether between two doubles bonds have respectively an average Mn close to 1,000 and 3,400. NANIO is a cross-linked copolymer of ethylene oxide/allyl glycidyl ether (EO/AGE) prepared by anionic initiation, while NVAN is a cross-linked EO/AGE copolymer initiated by Vandenberg initiators. The salt concentration is usually refered to the ratio O/Li in which O represents the ether solvating units and Li refer to the lithium salt. LiTFSI refers to $(CF_3SO_2)_2NLi$ in which the negative charge is well-delocalized on the electron-withdrawing groups, as evidenced by *ab initio* calculations [6]. In polymer electrolytes the glass transition temperature increases with salt concentration as exhibited by figure 2 which plots 1/Tg versus salt concentration. Thus a salt concentration increase reduces the segmental mobility while the number of charge carriers is increased. Therefore the evolution of conductivity with salt concentration is not linear and shows a maximum. With LiTFSI the slope of the plot is generally lower than with $LiClO_4$ and reaches here a value of 0.23 $K^{-1}.cm^3.mole^{-1}$.

It must be emphasized that these electrolytes can be shaped into thin films < 100 micrometers and have storage modulus higher than 2 MPa [7] on the rubbery plateau up to 80°C.

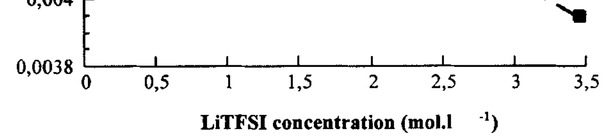


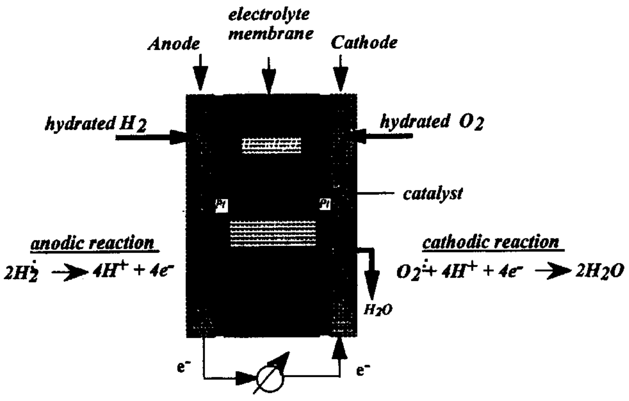
FIGURE 2 Tg^{-1} versus LiTFSI concentration in NPC 1000 polymer electrolyte.

Plasticized polymer electrolytes

Plasticized polymer electrolyte must be roughly considered as half-way between polymer electrolyte and separator. Indeed a mixture of liquid organic solvents swollens a polymer matrix and the content of liquid (in weight) is generally > 70%, but at the difference of polyolefine based separators the polymer interacts with the liquid electrolyte. Often described as new polymer electrolyte they have in fact preceded of about seven years the polymer electrolytes. Thus Feuillade [8] claimed in a french patent of 1973 the use of polyvinylformal swollen by organic solvents. In these plasticized polymer electrolytes the electrochemical stability remains mainly dependent on the liquid electrolyte. Plasticized polymer electrolytes, allowing the battery to be shaped in thin film [9], are well-adapted to lithium-ion batteries, in particular for cellular phones. Among the best polymer matrixes polyvinylidene fluoride - PVDF - polyacrylonitrile - PAN [10] - and poly(methylmethacrylate) PMMA. The previous conductivity comparison of our best polymer electrolytes with a plasticized electrolyte PAN/EC/PC/$LiClO_4$ shows that at low temperature the plasticized electrolyte is more conductive than the dry polymer electrolytes. On the other hand at 60°C the conductivities are very close. Taking into account that PAN plasticized electrolyte has very poor mechanical properties above 50°C, the ohmic resistance of a dry polyether electrolyte will be clearly lower from that temperature.

POLYELECTROLYTES AS MEMBRANE FOR PEMFC

Proton Exchange Membrane Fuel Cells should operate at moderate temperature, around 100°C, as compared to SOFC Solid Oxide Fuel Cell. So they appear as the more suited Fuel Cell for EV application. Below a PEMFC scheme:



The membrane consists in a proton-conducting polymeric material. The water production during the fuel cell working implies a water insolubility of the acidic functions. Therefore the membrane is often a polyelectrolyte. Unlike polymer electrolytes the protonic conductivity is strongly dependent on the water content (% of relative humidity) and resembles more to plasticized polymer electrolytes. The main characteristics of PEFMC membranes are :

- a high protonic conductivity > 10^{-2} S/cm in presence of water
- a thermal stability beyond the operating temperature > 100°C
- a chemical and electrochemical stability in acidic medium
- an impermeability to H_2 and O_2
- good mechanical properties
- above all a low cost.

Among the best membranes are the perfluorosulfonated membranes such as Nafion from Dupont de Nemours or Aciplex-S from Asahi Chemical Industry. Even in the event of a mass-production it seems however difficult to cut enough the price to meet the specifications of PEMFC. In order to keep a membrane based on a commercially available polymer we have selected polysulfones as polymer matrixes. The thermal stability of these thermoplastics is well-known. In addition one of their application deals with membranes, for instance ultrafiltration membranes. So we prepared sulfonated polysulfone by sulfonation with chlorosulfonic acid and trimethylsilylchlorosulfonate. Viscosimetry and Gel Permeation chromatography have shown that the use of chlorosulfonic reagent undergoes chain degradations, detrimental to the mechanical properties. On the contrary the chain lengths seem unaffected by the use of the other reagent. The latter allows the polysulfone to be sulfonated in a wide concentration range. The protonic conductivities increase with the sulfonation rate. Nevertheless, due to a dramatic water swelling at high sulfonation rate, the latter must be kept in the range 1.3 to 1.6 protons/kg. Thus, in order to keep a high conductivity while avoiding a loss in mechanical properties we proposed to use a polysulfonated polysulfone filled by an inorganic superprotonic conductor. The latter is a layered material belonging to the phosphatoantimonic acids $H_3Sb_3P_2O_{14},xH_2O$, abbreviated in H3. A synergic effect on conductivity has been evidenced when the filler is incorporated to sulfonated polysulfone PSS. The comparison of a filled and unfilled PSS shows a clear increase of the conductivity in PSS/ H3 [11]. Moreover the gas impermeability is improved by filling PSS with H3.

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