ELECTROCHEMICAL ANALYSIS OF SOLID POLYMER ELECTROLYTE MEMBRANES USED IN LITHIUM-BASED BATTERIES.

A literature survey.

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Polymer electrolyte membranes used in lithium batteries must possess some mechanical, chemical and electrical properties.

The electrochemical characterization of such polymer membranes implies mainly the determination of the **membrane ionic conductivity, the lithium transference number, and the electrochemical stability**.

1. Membrane conductivity

In order to be used as battery membrane, the polymeric material must be an electrical conducting separator. The conductivity is given not by the electron mobility but by the moving of the ions. Direct current measurements are therefore not applicable for measuring the electrical resistance and accordingly the ionic conductivity of the membrane. That is why the conductivity of the membrane is determined using alternating current, where no interface polarizations are occurring. Because of the periodic change of the electric field vector, the charge carrier accumulation is not produced and the current does not decrease with time. It is the case of impedance spectroscopy by applying a sinusoidal excitation voltage signal with low amplitude on the investigated sample. The answering signal is measured and the complex impedance is calculated over a wide frequency rage, usually from 1 Hz to 1 MHz. Two types of results plots are used for data analysis and the determination of the membrane resistance: Nyquist plots and Bode diagrams. The membrane ionic conductivity can be calculated by the formula:

$$\sigma = (1/R)(L/A),$$

where: R – the membrane resistance, L – the height of the sample between the electrodes, A – the cross-sectional contact area of the measured sample with the electrodes.

For experimental determination the polymeric membrane is fixed between the metal electrodes (stainless steel, gold, platinum, etc.). Swagelok cells are very suitable in this case.

The described method was applied for determination of polymer electrolyte ionic conductivities. This property of the membrane is crucial for its use in electrochemical cells, and especially in batteries. The target goal for battery membranes is 10^{-3} S/cm at room temperature. Some examples using this method are given in Table 1.

The ionic conductivities of the polymer electrolytes depend strongly on the composition and temperature. It can change between $10^{-2} - 10^{-8}$ S/cm [12].

Table 1.

Membrane	Conductivity (S/cm)	Ref.
Siloxane lithium ion conducting polymer electrolytes (poly{[3-[2,3(carbonyldioxy)propoxy]propyl] methylsiloxane)	10^{-7}-10^{-3} (7.99x10^{-3} at 25°C and 3.69x10^{-2} at 60°C)	1
Lewis-acid modified polymer LiBF$_4$/ ethylene carbonate + diethyl carbonate + triethylphosphate	4-6 x10^{-3} (the best values)	2
Poly (vinylidene fluoride-co-hexafluoropropylene)-based composite polymer electrolyte	10^{-3}–10^{-2}	3
P, O polymers (obtained from polyethylene glycols and organophosphates) containing lithium salts	1-4 x10^{-3}	4
Polyphosphonates with lithium perfluoromethyl sulfonimide as the ionic salt	0.6–1.0x10^{-3} at 22°C	5
Poly(ethylene imine) and lithium salts (LiF, LiCI, LiBr, Lil, LiSCN, LiClO$_4$ and LiBF$_4$)	10^{-8} (room temp.) 10^{-3} (150 °C)	6
Lithium-salt/poly(ethylene oxide)complex polymer electrolytes (LiCF$_3$SO$_3$-PEO$_x$ and LiClO$_4$-PEO$_x$)	10^{-3}	7
Cross-linked polysiloxanes containing oligoethylene oxide units, (OCH$_2$CH$_2$)$_n$, as internal free chains complexed with LiN(CF$_3$SO$_2$)$_2$ salt	2.50x10^{-5} to 1.62x10^{-4}	8
Ternary blends of poly(ethylene oxide), poly(bisphenol A-co-epichlorohydrin) and poly(vinyl ethyl ether), containing lithium perchlorate (LiClO$_4$)	10^{-4} - 10^{-3} S/cm (max 4.23x10^{-3}) (25°C)	9
Poly(oligo [oxyethylene] oxyterephthaloyl) and LiClO$_4$ penetrated into microporous polyethylene	3.2×10^{-4} (25°C)	10
Solid polymer electrolyte membranes prepared by photo-polymerisation of poly(ethyleglycol)methacrylic oligomers in the presence of a lithium salt	higher than 10^{-4} (60°C)	11

2. Transference number

Transference or transport number characterises the contribution of the charged particles present in the electrolyte to the charge transport across the electrochemical cell. It is a dimensionless parameter and it represents the fraction from the overall current transported by a particular charged species present in the electrolyte (ions and electrons).

For the determination of the transference number the Bruce & Vincent method [13] can be used. All necessary equipment will be prepared in a glove box. The cell used is in a symmetrical Li/electrolyte/Li configuration (lithium metal electrodes in a Swagelok type), assembled in glove box due to highly reactivity of metallic lithium towards air constituents. The EIS spectrum is recorded in range of frequencies of 1Hz-100kHz. Potentiostatic polarization to the cell is applied (potential should be in range of 10-20mV vs. lithium) and the current evolution is followed until a steady state is reached (sometimes it can take even tens of hours). After the stabilization of the current, the polarization is stopped and another impedance spectrum (similarly as before) is recorded. The transference number is then calculated using the Bruce-Vincent formula:

$$t_{Li} = I_{SS}(V-I_0R_0) / [I_0(V-I_{SS}R_{SS})],$$

where: t_{Li} – lithium transference number, V – applied potential, I_0 – initial current, I_{SS} – steady state current, R_0 – initial resistance of the passivation layer, R_{SS} – resistance of the passivation layer (steady state).

Some examples are given in Table 2.

Table 2.

Membrane	t_{Li}^+	Ref.
Poly (vinylidene fluoride-co-hexafluoropropylene)-based composite polymer electrolyte	0.3-0.5	3
Composite polymer electrolyte based on poly(ethylene oxide)–lithium tetrafluoroborate (addition of sulphatepromoted superacid zirconia)	0.42±0.05 (0.68±0.05 with S-ZrO_2)	14
Lewis-acid modified polymer ($LiBF_4$/ ethylene carbonate + diethyl carbonate + triethylphosphate)	~0.6	2
Copolymer electrolyte: poly(laurylmethacrylate) and PEO-based poly[oligo(oxyethylene)methacrylate] + polyethylene glycol dimethyl ether and doped with $LiCF_3SO_3$	0.5 (room temp.)	15
Poly(acrylonitrile)-based gels (using lithium salts like $LiN(CF_3SO_2)_2$)	> 0.5 (enhanced to 0.7)	12
Poly(methyl methacrylate) as polimer matrix and different electrolytes	0.2-0.7	12, 16

3. The electrochemical stability window

The electrochemical stability (decomposition voltage) of the polymer electrolyte membrane can be measured by linear sweep voltammetry. The working electrode is usually a stable metal electrode (platinum, stainless steel) or acetylene black, lithium metal being the counter and reference electrode.

The potentials for anodic oxidation (anodic stability) for some membrane electrolytes, obtained by linear voltammetry, are presented in Table 3. The electrochemical stability windows are sufficiently wide for using the membranes in lithium batteries. The high values make them to resist for overcharge abuse in rechargeable Li-based batteries, which have a high working voltage by itself.

Table 3.

Membrane	Anodic limit	Ref.
Poly (vinylidene fluoride-co-hexafluoropropylene)-based composite polymer electrolyte	> 4.7 V vs Li/Li$^+$	3
Polymers containing ethylene oxide groups linked with phosphate groups, $LiClO_4$	6 V vs Li/Li$^+$	4
Microporous polyethylene with highly conductive solvent-free polymer electrolyte based on poly(oligo [oxyethylene] oxyterephthaloyl)	> 4.4 V vs Li/Li$^+$	10
Solid polymer electrolyte membranes prepared by photo-polymerisation of poly(ethyleglycol)methacrylic oligomers in the presence of a lithium salt	5 V vs Li/Li$^+$	11
Copolymerization of methylmethacrylate monomer onto polyethylene separator	4.6 V vs Li/Li$^+$	17
Poly(lauryl methacrylate)-*b*-poly[oligo(oxyethylene) methacrylate]-based block copolymer electrolytes	~4 V vs Li/Li$^+$	15

ACKNOWLEGEMENTS

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