Russian Chemical Reviews **81** (4) 367 – 380 (2012) © 2012 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2012v081n04ABEH004210

Polymer gel electrolytes for lithium batteries

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Abstract. The data on the most promising polymer gel electrolytes for lithium batteries published in the past decade are surveyed and described systematically. Gel electrolytes with matrices of polyethylene oxide, poly(vinylidene fluoride) and its copolymer with hexafluoropropylene, poly(methyl methacrylate), polyacrylonitrile, poly(vinyl chloride) and polyacrylates are discussed. A special section is devoted to gel electrolytes with ionic liquids as the solvents. The bibliography includes 160 references.

I. Introduction

The studies aimed at the development of rechargeable lithium cells have been carried out for more than 30 years. Lithium metal exhibits the highest theoretically possible specific capacity (3.86 A h g^{-1}); however, operation of rechargeable batteries with lithium anodes is complicated by several factors, namely, explosion or ignition hazard due to non-uniform cooling of lithium to form acicular structures (dendrite formation) on the anode surface in the course of charge – discharge processes in the battery.[1–3] This is why in the early 1990s, the Sony company (Japan) started the production of the so-called lithium-ion batteries with the anode of a carbon material capable of incorporating lithium ions.[4] During charging, Li^+ ions migrate from the cathode through the electrolyte to the anode and penetrate into the carbon structure; the reverse processes occur at the discharge (Fig. 1).[5]

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Received 14 February 2011
Uspekhi Khimii **81** (4) 367 – 380 (2012); translated by T Ya Safonova

Thus, the overall current-determining reaction taken place on both electrodes implies continuous transfer of lithium ions through the electrolyte:

$$LiMO_2 + C_n \rightleftharpoons Li_{1-x}MO_2 + Li_xC_n. \quad (1)$$

Apart from anodic and cathodic materials, the key components that determine the power intensity of the system include the electrolyte. Lithium ion batteries traditionally use liquid electrolytes, *i.e.*, lithium salt solutions in aprotic organic solvents with the high ionic conductivity ($\sim 10^{-2}$ S cm^{-1}) at room temperature. However, the electrode reactions can be accompanied by electrolyte decomposition or its loss due to the lithium cell leakage. The use of a polymer electrolyte in place of the liquid electrolyte helps to solve several problems. Lithium-polymer batteries are safer in operation, more compact and can be prepared in any configuration in soft casings.

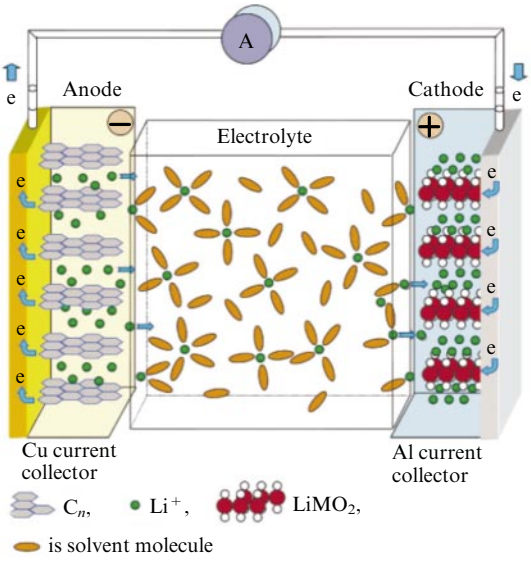


Figure 1. Illustration of the lithium ion battery operation (discharge).[5]

Studies of poly(ethylene oxide) (PEO) complexes with lithium date back to 1973[6] but their practical value was understood only later. In 1978, Armand *et al.*[7] (see †) proposed to use the PEO–lithium-salt system as a solid electrolyte. However, the ionic conductivity of this system was very low ($\sim 10^{-8}$ S cm^{-1} at room temperature). The introduction of an organic aprotic dipolar solvent (plasticizer) into this system favours the increase in its conductivity up to 10^{-4}–10^{-2} S cm^{-1}; this is accompanied by the formation of polymer gel electrolytes.[8]

The plasticizer solvents solvate Li^+ ions, thus facilitating their transport. The solvents containing carbonyl or ether groups, which are capable of dissolving large amounts of lithium salts,[9] such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC) and γ-butyrolactone (GBL), are used most widely. In the majority of cases, very different and often controversial requirements are imposed on plasticizers for polymer gel electrolytes, which include a high dielectric permittivity and, in contrast, a low viscosity. Individual solvents fail to completely fulfil these requirements; this is why electrolytes are prepared by using mixtures of solvents.

The salts $LiBF_4$, $LiPF_6$, $LiAsF_6$, $LiClO_4$, $Li(CF_3SO_3)$, $LiN(CF_3SO_2)_2$ and $LiN(C_2F_5SO_2)_2$ are used most frequently as the electrolytes. The electrolyte compositions from different manufacturers of commercial lithium-ion batteries differ from one another. The most frequently used components are $LiPF_6$ as the salt, EC as the solvent and DMC, DEC and EMC as the co-solvents. At the same time, the quest for new electrolyte components and various additives capable of modifying the existing compositions never ceases. The new solvents are used largely for improving the operation of polymer gel electrolytes at low temperatures and the new salts are destined for increasing their thermal stability. The additives are introduced mostly to improve the interfacial properties of the electrode–electrolyte system[5] and enhance the safety of lithium batteries.[10–13]

Polymer matrices for gel electrolytes should provide the high mechanical stability of the final product and also be compatible with the liquid electrolyte. Table 1 shows polymers used most often as the matrices for polymer gel electrolytes.

The presence of heteroatoms arranged in a definite order in a polymer chain favours the transport of Li^+ ions and thus increases the gel electrolyte conductivity. The melting and glass transition temperatures should lie beyond the range of working temperatures of the battery.

The following two classes of gel electrolytes can be distinguished: heterogeneous (phase-separated) and homogeneous (uniform). Heterogeneous gels represent a polymer framework with the system of interconnected pores filled with electrolyte. Thus, the preparation of heterogeneous gel electrolytes includes two stages: the formation of a porous polymer membrane and its activation with a liquid organic electrolyte. The compositions used to prepare homogeneous gel electrolyte films represent mixtures of a polymer and a lithium salt solution in an aprotic organic solvent, *i.e.*, the electrolyte is being incorporated into the polymer matrix at the molecular level.

† See also in M Armand *Solid State Ionics* **69** 309 (1994).

Table 1. Glass transition (T_g) and melting (T_m) temperatures of polymer matrix for gel electrolytes.[14]

Polymer	Polymer unit	T_g/°C	T_m/°C
PEO	CH_2CH_2O	−60	65
PVDF	CH_2CF_2	−30	170
PMMA	$CH_2C(Me)(CO_2Me)$	120	–
PAN	$CH_2CH(CN)$	90	–
PVC	CH_2CHCl	80	220

Note. From here on, the following abbreviations are used: PVDF is poly(vinylidene fluoride), PMMA is poly(methyl methacrylate), PAN is polyacrylonitrile, PVC is poly(vinyl chloride).

To date, a large number of polymer gel electrolytes incorporating lithium salts and plasticizing organic solvents were proposed.[15,16] To be successfully used in practice, the gel electrolytes should be mechanically stable, capable of holding the liquid electrolyte thus preventing its escape, electrochemically resistant to the anode and cathode materials and also possess a high ionic conductivity in a wide temperature range.

Polymer gel electrolytes play an important role in the development of electrochemical devices, being the most suitable materials for lithium-ion batteries and batteries with anodes of metal lithium. The present review summarizes the results on gel electrolytes based on matrices made of PEO, PMMA, PAN, PVC and PVDF and its copolymer with hexafluoropropylene (HFP) and also on polyacrylate systems published in the past 10 years. Their physical and electrochemical properties and also the advantages and specific features of their use in lithium batteries are analyzed and an attempt is undertaken to systematize the methods used for preparation of gel electrolytes and modification of polymer matrices.

II. Gel electrolytes based on polymer matrices

1. Gel electrolytes based on poly(ethylene oxide)

Polymer electrolytes based on poly(ethylene oxide) are the most thoroughly studied systems. The majority of publications are devoted to PEO–Li^+ complexes in the absence of solvent. The latter systems exhibit the ionic conductivity in the range from 10^{-8} to 10^{-4} S cm^{-1} at temperatures from 40 to 100 °C, which rules out their practical use at room temperature. The plasticized PEO-based polymer electrolytes exhibit a high conductivity as a result of their lower degree of crystallinity.[17]

A considerable increase in the conductivity (10^{-3}–10^{-4} S cm^{-1} at 25 °C) as compared with a solid polymer electrolyte was demonstrated by PEO films plasticized with $Li(CF_3SO_3)$–PC,[18] $LiClO_4$–EC–DEC[19] and $LiBF_4$–EC–GBL[20] liquid electrolytes.

Kucharski *et al.*[21] prepared the 15 PEO–40 PC–40 EC–5 $LiClO_4$ (wt %) composition as follows: PEO was dissolved in acetonitrile and the salt was dissolved in the mixture of plasticizers, then these solutions were mixed together to obtain a homogeneous solution from which the polymer gel electrolyte film was cast. The electrolyte demonstrated a conductivity of 10^{-4} S cm^{-1} at room temperature. As the salt concentration increased to 10 wt %, the conductivity increased to 6.4×10^{-3} S cm^{-1} but the

mechanical properties were impaired due to inadequate gel formation.

Basumallick *et al.*[22] synthesized a gel electrolyte based on PEO and a 1 M $LiClO_4$ solution in dimethylformamide (DMF) saturated with LiOH and Li_2SO_3. The latter additives were beneficial for the formation of the solid electrolyte interface (SEI) layer on the anode surface. The gel conductivity at room temperature was 10^{-4} S cm^{-1} and increased with the increase in the temperature. The discharge capacity of the C/polymer gel electrolyte/$LiCoO_2$ cell was stable at cell cycling in the interval of 2.5–4.0 V.

Zaghib *et al.*[23,24] studied the performance characteristics of C/polymer gel electrolyte/$LiFePO_4$ cells. As the matrix, PEO was taken; the liquid electrolytes represented 1.5 M $LiN(FSO_2)_2$ solutions in the EC–GBL (1 : 3 by volume) and EC–PC–DMC (1 : 1 : 3 by volume) solvent mixtures. Gel electrolytes were synthesized by the radiation- and thermally induced polymerization. In the first case, the polyether components were cross-linked by exposure to an electron beam to produce a polymer matrix, which was later impregnated with a liquid electrolyte. The second polymer electrolyte was obtained by mixing PEO with liquid organic electrolytes in a 10 : 90 volume ratio in the presence of a thermal polymerization initiator. This mixture was spread over electrodes and introduced into a polypropylene separator; then, the cells were assembled and heated to 60 °C for 1 h to complete the cross-linking and gel electrolyte formation processes. The ionic conductivity of a gel electrolyte based on 1.5 M $LiN(FSO_2)_2$ was higher for the use of the EC–GBL mixture as compared with the EC–PC–DMC mixture, being equal to 10^{-3} S cm^{-1} at 20 °C. For an anode made of natural graphite, a high specific capacity ($\sim$360 mA h g^{-1}) and a high Coulombic efficiency of charge–discharge ($\sim$92%) were observed; for a $LiFePO_4$ cathode, the capacity was $\sim$160 mA h g^{-1} and the Coulombic efficiency was $\sim$93%. A lithium-ion battery with these gel electrolytes demonstrated a very low loss in capacity (5%) after 500 charge–discharge cycles.

The CH_2CH_2O unit in the PEO chain exhibits good solvating ability with respect to Li^+ ions. In the gel electrolyte, the polymer chain segments are highly mobile. By modifying the PEO structure (introduction of substituents that decrease the chain regularity, the synthesis of branched, comb-like and network polymer matrices), one can enhance the conductivity of the corresponding gel electrolytes.[25,26]

2. Gel electrolytes based on poly(vinylidene fluoride) and its copolymer with hexafluoropropylene

Poly(vinylidene fluoride) and its copolymer with hexafluoropropylene (PVDF-HFP) meet all the requirements on polymer matrices for gel electrolytes.[27,28] Due to the presence of strong electron-withdrawing functional C–F groups in their structure, these polymers are characterized by electrochemical stability and incombustibility. Moreover, they have high dielectric permittivity, which promotes better ionization of lithium salts and provides a considerable concentration of charge carriers. When these polymers are used as gel electrolytes, the most important aspect is their resistance to metal lithium. On the Li anode, the interfacial reaction of Li^+ with the C–F group proceeds to form LiF; this is why polymer electrolytes based on PVDF and its copolymer are used in lithium-ion batteries with carbon anodes.

The PVDF-HFP copolymer is used more often than PVDF as the polymer matrix for gel electrolytes, because the presence of HFP units results in a lower degree of crystallinity and greater absorption of liquid electrolyte. The PVDF-HFP copolymer with the HFP content of 12 mol % – 19 mol % ('Kynar Flex', 'Solef', F-26) has a semicrystalline structure, T_m = 130–140 °C and T_g from −40 to −35 °C; when the HFP content is higher, the copolymer ('Fluorel', 'Viton A', SKF-26) exhibits the properties of a completely amorphous elastomer with T_g from −22 to −29 °C (Ref. 29).

The first films of gel electrolytes based on PVDF and PVDF-HFP were prepared by casting from solution to afford a homogeneous gel electrolyte. The polymer matrix was dissolved in a low-boiling-point solvent [*e.g.*, acetone, tetrahydrofuran (THF), acetonitrile] together with a non-aqueous electrolyte containing a lithium salt. The resulting viscous solution was applied on a glass support to form a gel.[30] The thus formed gel electrolyte films demonstrated high ionic conductivities; however, as a rule, they were sticky and mechanically unstable, these drawbacks preventing their use.

In the mid-1990s, the Bellcore company [now known as Telcordia Technologies (USA)] put forward a procedure for the preparation of heterogeneous polymer gel electrolytes based on PVDF-HFP.[31] This marked the beginning of the active research of these systems.

Tarascon *et al.*[32] have proposed the following procedure. First of all, they dissolved PVDF-HFP in acetone and then added dibutyl phthalate (DBP) as a plasticizer containing no lithium salts. After evaporation of the solvent, the plasticized polymer films were obtained. Then, the plasticizer was extracted into an appropriate solvent (dimethyl ether, methanol). After the removal of DBP, a porous structure was formed in polymer layers to be filled with a liquid organic electrolyte in the next stage. Thus, as a result of activation, the membrane swells and transforms into a gel electrolyte. The ionic conductivity of the gel electrolyte based on PVDF-HFP and a 1 M $LiPF_6$ solution in EC–PC was 2×10^{-4} S cm^{-1} at room temperature, but the amount of absorbed electrolyte turned out to be somewhat lower than the amount needed to fill the original volume occupied by DBP. This method has its drawbacks associated with safety when dealing with large volumes of volatile solvents.

Polymer membranes should have a good porous structure (porosity of $\sim$80%, the pore diameter $<$1 μm).[33] Currently, phase inversion and electrospinning methods are widely used to prepare porous membranes. Among the phase inversion methods, the following methods can be mentioned:

— nonsolvent-induced phase separation/inversion (NIPS);

— evaporation-induced phase separation/inversion (EIPS);

— thermally induced phase separation/inversion (TIPS).

The EIPS process makes it possible to avoid the stage of plasticizer removal. The solutions for casting the film contain the following three components: a polymer, a solvent and a pore-formation agent, *i.e.*, nonsolvent. The nonsolvent should be less volatile than the solvent. The evaporation of the solvent and the pore-forming agent produces a porous membrane, which is later impregnated with a liquid organic electrolyte.[34,35]

Thus, Aravindan *et al.*[36] used acetone as the solvent and ethanol as the nonsolvent. The membrane was activated with a 0.5 M $LiPF_3(CF_2CF_3)_3$ solution in EC–DEC (1 : 1 by weight). The ionic conductivity of synthesized gel electrolytes was 1.57×10^{-3} S cm^{-1} at room temperature. The mechanical stability of PVDF-HFP membranes and PVDF-HFP–$LiPF_3(CF_2CF_3)_3$–EC–DEC gel electrolytes was studied. Their Young's moduli were 4.3 and 4.1 MPa, respectively.

The use of the EIPS method allows one to easily control the membrane structure by selecting various solvents and pore-forming agents.[37, 38]

In another study,[39] the PVDF-HFP copolymer and poly(vinyl alcohol) were dissolved in DMF. The resulting viscous solutions were spread over a glass support. The films obtained after the DMF evaporation were immersed into deionized water (at 60 °C) to remove poly(vinyl alcohol) and remaining DMF from the PVDF-HFP matrix. This served to produce a microporous structure. The ready membranes were dried under reduced pressure at 80 °C for 5 h. Membranes based of the PVDF-HFP copolymer and prepared by this procedure had the high degrees of porosity (85.9%) and electrolyte uptake (89.6%); the ionic conductivity of the polymer gel electrolyte prepared by activation with a 1 M $LiClO_4$ solution in EC–DEC (1 : 1 volume ratio) reached 7.94×10^{-3} S cm^{-1} at 25 °C.

A membrane based on the PVDF-HFP copolymer was prepared[40] by the EIPS method with the use of three different solvents (THF, acetone and DMF) and poly(ethylene glycol) (PEG) as the pore-forming agent. When DMF was used as the solvent, the resulting matrices had rougher morphology and a smaller number of pores. The increase in the PEG content increased the degree of porosity of membranes, which in turn increased the amount of absorbed liquid electrolyte and enhanced the ionic conductivity. However, the introduction of >50 wt % PEG resulted in its escape from the finished PVDF-HFP membrane. In the same study, the cycling of Li/polymer gel electrolyte/$LiCoO_2$ cells was considered. The loss of sample capacity after 50 cycles was ~10%–11%. Moreover, the cells containing a gel electrolyte based on a 50 wt % PVDF–50 wt % PEG (acetone as the solvent) membrane and a 1 M $LiPF_6$ solution in EC–DEC (1 : 1 by volume) with the maximum electrolyte uptake (115% relative to the dry membrane weight) demonstrated the minimum capacity. Evidently, due to the compact assembling of cells, a part of electrolyte was forced out from the membrane.

When a porous membrane is prepared by the TIPS method, the polymer is first dissolved at a high temperature and the resulting solution is cooled to induce the phase inversion.[41, 42] Thus, a microporous PVDF membrane for gel electrolytes was prepared by the TIPS method with the use of a mixture of solvents, namely, DBP and di(2-ethylhexyl) phthalate (DEHP).[43] By varying the DBP and DEHP ratio in the mixture, one can easily control the membrane porous structure.

Chiu *et al.*[44, 45] carried out a series of studies on the synthesis of porous PVDF-HFP membranes by the TIPS method. The polymer (20 wt %–35 wt %) was dissolved in sulfolane at 160 °C and the resulting solution was kept in liquid nitrogen. The films were prepared by the mould pressing on heating; sulfolane was extracted into water and ethanol to obtain the porous structure. The ready membranes were vacuum dried for the removal of solvent traces and then impregnated with a 1 M $LiPF_6$ solution in the EC–DMC–EMC solvent mixture (1 : 1 : 1 by weight). Studies of the polymer matrix morphology have demonstrated the presence of spherulites and the network regions containing pass-through chains. The pores between spherulites were interconnected, which had a beneficial effect on the Li^+ ion migration in the polymer gel electrolyte. A decrease in the copolymer content in the PVDF-HFP–sulfolane composition increased the share of network regions, simultaneously decreasing the degree of crystallinity and increasing the degrees of porosity and liquid electrolyte absorption. The maximum ionic conductivity was 2.93×10^{-3} S cm^{-1} (20 °C), the electrolyte uptake was 182.1%, the transport number of lithium ions was 0.55. The polymer gel electrolytes were electrochemically stable up to 4.7 V (*vs.* Li/Li^+).

Membranes synthesized by the electrospinning method proved to be especially suitable for their use as the absorbing matrices in microporous polymer electrolytes. Nonwoven fibrous materials with a high surface area can operate as efficient ion-conducting channels.[46, 47] Under the effect of electrostatic forces generated by a high-voltage source, ultrathin filaments (nanofibres) can be spun from a polymer solution.[48, 49] The first information on the PVDF- and PVDF-HFP-based membranes formed by the electrospinning method and used in lithium-ion batteries appeared in 2003.[50]

Kim *et al.*[51] prepared fibrous PVDF-HFP membranes by electrospinning from the copolymer dissolved in acetone and *N*,*N*-dimethylacetamide (7 : 3 by weight). The initial mixture was loaded into a needle (inner diameter of 0.3 mm) to which a voltage of 15 kV was applied. Fibres were placed on a polished stainless-steel collector; the distance between the collector and the needle was 12 cm. The resulting fibromembranes were vacuum dried at 80 °C to remove the remaining solvents. The ready membrane had a smooth surface, the average fibre diameter was 0.5 μm and the average size of pores between the fibres was 1.8 μm. The polymer electrolyte was prepared by soaking the membrane in a 1 M solution of $LiPF_6$ in EC–DMC–DEC (1 : 1 : 1 by weight); it had the conductivity of 1×10^{-3} S cm^{-1} at room temperature and was electrochemically stable up to 4.5 V (*vs.* Li/Li^+).

Polymer gel electrolytes based on electrospinned PVDF membranes and 1 M solutions of $LiPF_6$ in EC–DMC, EC–EMC and EC–DEC (1 : 1 weight ratio) were shown[52] to exhibit good electrochemical properties. The C/$LiCoO_2$ cells with these electrolytes displayed adequate cyclability. Their discharge capacity after 80 cycles at a rate of 0.5 *C* (see ‡) was ~60% of the initial discharge capacity.

In microporous gel electrolytes based on PVDF and the PVDF-HFP copolymer, at least two main parts can be distinguished: micropores filled with the liquid electrolyte and the amporphous part plasticized with the electrolyte solution. If the main membrane volume consists of interconnected micropores, then the ionic conductivity of the polymer gel electrolyte is determined by the liquid electrolyte properties. For a membrane with a small number of pores, the transfer of Li^+ ions largely proceeds in the plasticized regions. Hence, the increase in the membrane porosity and the changes in the polymer matrix crystallinity

‡ *C* is the charging (or discharging) current numerically equal to the current source capacity at its complete discharge for 1 h.

are the decisive factors in the preparation of mechanically stable heterogeneous gels with the high Li^+ conductivity. Gels with the mentioned properties can also be prepared by modification (mixing, cross-linking, copolymerization) of the polymer matrix.

Mixing of flexible-chain conducting polymer components with a mechanically stable polymer increases the conductivity and mechanical stability. The following polymers are suitable for mixing with PVDF or PVDF-HFP: PEO, PAN, PMMA and their copolymers.[53–55]

Cui *et al.*[56,57] mixed PVDF with the PEO-PPO-PEO copolymer [PPO is poly(propylene oxide)] and PMMA. The polymer matrices were prepared by the TIPS method. To obtain gel electrolytes, a 1 M $LiPF_6$ solution in the EC–DMC–EMC mixture (1:1:1 by weight) was used. The ionic conductivity increased with the increase in the PEO-PPO-PEO and PMMA contents, because mixing of polymers induced the formation of interconnected pores of definite sizes. Pores are the main 'reservoirs' for the liquid electrolyte storage. This is evidenced by the linear temperature dependence of conductivity $\log\sigma$ *vs.* $1000/T$ for all polymer electrolytes in the temperature range of 0–80 °C.

Fibrous PVDF–PAN membranes with different PAN contents (25 wt %, 50 wt % and 75 wt %) were prepared by electrospinning.[58] As the solvent, the mixture of DMF and acetone (7:3 by volume) was used. The polymer solution was supplied to a capillary by means of a pump, the distance between the capillary and the collector was 20 cm and the potential difference between them was 25 kV. The uptake of the 1 M $LiClO_4$ solution in EC was ~300% of the dry fibromembrane weight. The polymer gel electrolyte based on PVDF-HFP–PAN (25 wt %) exhibited the conductivity of 7.8×10^{-3} S cm^{-1} at room temperature and was electrochemically stable up to 5.1 V (*vs.* Li/Li^+). The addition of PAN to the system decreased the resistance at the Li/gel electrolyte interface.

Highly porous membranes can absorb large amounts of liquid electrolyte and the resulting polymer gel electrolytes exhibit high ionic conductivity but their mechanical properties are inadequate. This problem can be solved by the microphase separation of polymers and the formation of interpenetrating polymer networks.

For modifying the PVDF-HFP-based matrix, Ren *et al.*[59] used the addition of diepoxypolyethylene glycol (DEPEG) and polyethyleneimine (PEI) as the oligomer and the cross-linking agent, respectively. In the process, PVDF-HFP was mixed with DEPEG + PEI in different ratios [(80:20–20:80) wt %], and membranes were prepared by the phase inversion method. Heating of the prepared membranes induced cross-linking between the terminal epoxy groups of DEPEG and the amino groups of PEI to form a three-dimensional network. The fact of cross-linking was confirmed in IR spectroscopic studies, being indicated by a decrease in the intensity of peaks corresponding to epoxy groups. The individual polymers were not bound chemically; nevertheless, they could not be separated due to mechanical intertwining between the PVDF-HFP chains and the network. Gel electrolytes were prepared by soaking the matrix in a 1 M $LiPF_6$ solution in the EC–DMC (1:1 by weight) mixture. For a gel electrolyte with the 60 PVDF-HFP–40 (DEPEG + PEI) (wt %) composition, the maximum ionic conductivity was 2.3×10^{-3} S cm^{-1} at 20 °C. Moreover, polymer gel electrolytes of all compositions were electrochemically stable up to 4.8 V (*vs.* Li/Li^+).

Zhao *et al.*[60] modified an electrospun PVDF-HFP membrane with poly(ethylene glycol dimethacrylate) (PEGDMA). The prepared fibromembranes were vacuum dried for 12 h to remove the solvent traces and then heated to 125–130 °C to induce the PEGDMA cross-linking. Studying the membrane surface by a scanning electron microscope has shown that fibres in the PVDF-HFP–PEGDMA (4:1 by weight) composition have virtually the same morphology before and after polymerization. The addition of PEGDMA induced an increase in the mechanical stability and flexibility of the polymer matrix. The porosity and liquid electrolyte uptake (1 M $LiPF_6$ solution in EC–DMC–EMC with the 1:1:1 by weight) by the PVDF-HFP–PEGDMA membrane (4:1 by weight) were $70.0\pm1.6\%$ and $267\pm11\%$, respectively. The conductivity of the polymer gel electrolyte was 2.82×10^{-3} S cm^{-1} at room temperature.

Gel electrolytes based on PVDF and PVDF-HFP exhibit fairly high ionic conductivity. However, for their practical use in lithium batteries, their cost and the overall yield of their synthesis are also important.

3. Gel electrolytes based on poly(methyl methacrylate)

Whereas PVDF and PVDF-HFP are used mainly in the preparation of microporous membranes which are later activated with a liquid organic electrolyte, the use of PMMA is associated with the preparation of homogeneous gels by the methods of casting from solutions and polymerization with different initiation types.

According to a review,[61] Iijima *et al.*§ were the first to propose in 1985 the use of PMMA in the preparation of polymer gel electrolytes. The conductivity of the synthesized gel which contained 15 wt % PMMA with the average molecular weight of 7000 was of the order of magnitude of 10^{-3} S cm^{-1} at 25 °C.

In several publications by Sekhon *et al.*,[62–65] the gel electrolytes containing up to 25 wt % PMMA and lithium salts LiX [X = ClO_4, CF_3SO_3, $N(CF_3SO_2)_2$] dissolved in aprotic (PC, EC, GBL) and binary (PC + EC, PC + GBL, EC + GBL) solvents were prepared. The influence of the salt and the solvent on the properties of polymer gel electrolytes was studied, as well as the role of polymers in the mechanism of ionic conduction. The addition of PMMA to lithium-conducting electrolytes entailed an increase in the solution viscosity and a decrease in its conductivity. It was shown that the polymer plays a passive rather than the solvating role in these systems. The temperature dependences of the conductivity and viscosity of liquid and gel electrolytes demonstrated one and the same tendency (Figs 2 and 3). The conduction mechanism in PMMA-based gel electrolytes is the same as in liquid electrolytes, but the polymer matrix imparts mechanical stability to gels making easier the cell fabrication. For all systems, the maximum conductivity at 25 °C was ~10^{-3} S cm^{-1}. The highest conductivity was exhibited by a gel electrolyte containing the $LiN(CF_3SO_2)_2$ salt in a concentration of 1 mol litre^{-1}. The conductivity of polymer gel electrolytes with solvents under study increased in the following series:

$$PC < PC + EC < PC + GBL < EC + GBL < GBL < EC.$$

§ See T Iijima, Y Toyoguchi, N Enda *Denki Kagaku* **53** 619 (1985).

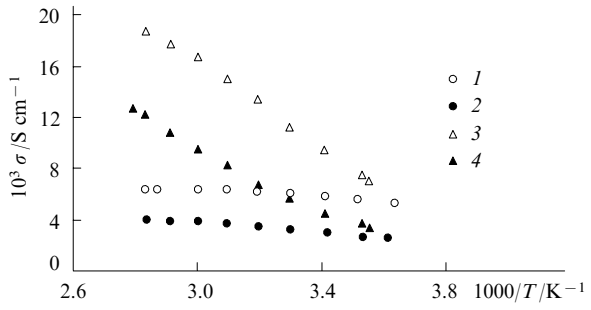


Figure 2. Temperature dependences of the conductivity (σ) of 1 M $LiN(CF_3SO_2)_2$ solutions in PC containing 0 wt % (*1*) and 10 wt % (*2*) PMMA and also in EC – PC (1 : 1 by volume) containing 0 wt % (*3*) and 10 wt % (*4*) PMMA.[63]

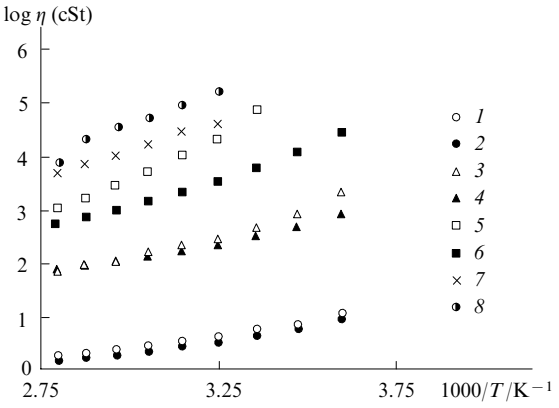


Figure 3. Temperature dependences of the viscosity (η) of 1 M $LiClO_4$ (*1*, *3*, *5*, *7*) and $LiN(CF_3SO_2)_2$ (*2*, *4*, *6*, *8*) solutions in EC – PC (1 : 1 volume ratio) with 0 (*1*, *2*), 5 (*3*, *4*), 10 (*5*, *6*) and 15 (*7*, *8*) wt % PMMA.[63]

Hashmi *et al.*[66] studied gel electrolytes based on the PMMA – EC – EC – $LiClO_4$ system. The polymer was added to the liquid electrolyte, the mixture was heated to 70 °C for 10 – 12 h and then slowly cooled to room temperature. Thermoplastic atactic PMMA with $T_g \approx 114$ °C was used, which served as a matrix for the liquid electrolyte. The ionic conductivity of the gel decreased with the increase in the amount of added polymer component. After the addition of < 20 wt % PMMA, only a part of liquid electrolyte was involved in the gel formation, and the polymer gel electrolyte represented a viscous solution; the addition of > 20 wt % PMMA resulted in the formation of a very tough film with a low ionic conductivity. Hence, the optimal composition of the gel electrolyte is as follows: 20 wt % PMMA – 80 wt % 1 M $LiClO_4$ in EC – PC (1 : 1 by volume); at room temperature, its conductivity is 10^{-3} S m^{-1}.

Ramesh and Ang[67] have prepared plasticized polymer electrolytes based on PMMA and $LiN(CF_3SO_2)_2$ with PC and EC additives by solution casting method. They used THF as the solvent, which was later evaporated to obtain a film. The analysis of FT-IR spectra has revealed no chemical reactions between the polymer, the plasticizer and the salt and, presumably, only physical interactions took place due to the formation of ion pairs and aggregates (the superposition and broadening of the absorption bands for the C=O group at 1785 and 1765 cm^{-1}). The maximum ionic conductivity at room temperature was observed for compositions containing 20 wt % EC in the PMMA – $LiN(CF_3SO_2)_2$ – EC system and also 30 wt % PC in the PMMA – $LiN(CF_3SO_2)_2$ – EC – PC system, namely, 1.28×10^{-4} and 2.00×10^{-4} S cm^{-1}, respectively.

Gel electrolytes containing PMMA, PC and a lithium salt ($LiClO_4$, $LiBF_4$) were studied in detail.[68,69] These polymer gel electrolytes were synthesized by thermal polymerization in the presence of benzoyl peroxide (BP) and 2,2′-azobis(isobutyronitrile) (AIBN). The resulting homogeneous gels demonstrated fairly good ionic conductivity ($10^{-3} - 10^{-4}$ S cm^{-1}) in a wide temperature range.

Zhou *et al.*[70,71] synthesized gel electrolytes based on methyl methacrylate (MMA) and a liquid electrolyte containing 1 M $LiPF_6$ in EC – DEC (1 : 1 by weight) by *in situ* thermal polymerization and γ-radiation-induced polymerization in CR 2032 cells. A precursor of the polymer gel electrolyte was applied on a porous polypropylene separator and then rechargeable cells with $LiNi_{0.8}Co_{0.2}O_2$ cathodes and graphite anodes were assembled. Thermal polymerization was carried out in the presence of an initiator (BP) at 70 °C for 2 – 4 h. The radiation-induced polymerization needs no initiator; hence, the produced polymer gel electrolytes are of the high purity grade. Under the action of γ-radiation, the active sites are created in the monomer; this process occurs throughout the entire volume at any temperature. The gel electrolyte in question exhibited the ionic conductivity of $> 10^{-3}$ S cm^{-1} at room temperature and was electrochemically stable up to 4.2 V (*vs.* Li/Li^+). The specific discharge capacity of the $LiNi_{0.8}Co_{0.2}O_2$/polymer gel electrolyte/C cells reached ~180 mA h g^{-1}. After the first cycle, the capacity loss of *ca.* 100 mA h g^{-1} was observed but further cycling was reasonably good. The capacity loss can be explained by the formation of a SEI layer on the graphite anode (~35 mA h g^{-1}) and the interaction of a Li^+ cation with a CO_2Me group that remained after MMA on the cathode (~65 mA h g^{-1}).

It is difficult to obtain strong elastic films of polymer gel electrolytes with sufficient ionic conductivity by solution casting method. This problem can be solved by polymerization. In addition, numerous studies (for example, see Refs 72–74) were devoted to modifying the PMMA-based polymer matrix in order to increase the thermal and mechanical stability of the ready film, enhance its ionic conductivity and improve the transport properties of gel electrolytes.

By mixing two (or more) polymers one can obtain a new polymer with the desired properties. Polymer gel electrolytes based on the PMMA – poly(vinyl acetate) (PVA) mixture with the 3 : 1 weight ratio, $LiClO_4$ and PC were studied.[75] The required amounts of components were dissolved in anhydrous THF and mixed to obtain a homogeneous mass. Then, the solution was left for 48 h at room temperature for the slow evaporation of the solvent. The gel electrolytes were studied by X-ray diffraction, scanning electron microscopy, thermogravimetry and Fourier transform IR spectroscopy. All tested electrolytes demonstrated sufficiently high ionic conductivity; the 25 (PMMA + PVA) – 67 PC – 8 $LiClO_4$ (wt %) composition demonstrated the maximum conductivity (4.5×10^{-3} S cm^{-1} at 30 °C) and good mechanical stability.

The addition of large amounts of polymer increases the mechanical stability of the film but severely affects its

conductivity. A minimum amount of polymer component can hold the liquid electrolyte only if various network structures are formed.

Kim and Oh [76] reported on the mechanical stability and ionic conductivity of polymer gel electrolytes based on PMMA modified with the interpenetrating polymer network components. Their components, namely, PMMA, PEGDMA, $LiClO_4$ and EC, were mixed to obtain a homogeneous solution, cast on glass supports and then irradiated with UV light for cross linking PEGDMA (initiation with BP). Samples of PEGDMA with different numbers (n) of repeating ethylene oxide units ($n = 4.0, 8.7, 16.4$) were used for modification. The strongest film was obtained for $n = 4.0$, because the cross-linking density is inversely proportional to the polymer molecular mass. For the overall content of PMMA + PEGDMA of 30 wt %, a stable gel electrolyte film could be obtained, whereas for gels containing individual PMMA, the films could be obtained only after the addition of 50 wt % polymer. The PEGDMA chain is more flexible as compared with PMMA; this is why, the mobility of Li^+ ions increased together with the ionic conductivity [σ_{max} (25 °C) $\approx 10^{-3}$ S cm^{-1}].

Thus, the PMMA polymer matrix loses its stability on plasticizing; hence, to be used in practice, it should be reinforced by chemical or physical methods.

4. Gel electrolytes based on polyacrylonitrile

Polyacrylonitrile is one of the polymers used most widely as matrices in the preparation of heterogeneous and homogeneous gels. Many studies were devoted to these matrices (for example, see Refs 77–79).

Being involved in polymer gel electrolytes, PAN can play different roles in the mechanism of lithium ion transfer. The polymer matrix serves not only as a framework that reinforces the gel electrolyte structure but it also may take part in the transport of Li^+ ions.[80] The vibrational spectroscopy studies of these systems have shown that their Raman spectrum contains an absorption band at 2265 cm^{-1}, which corresponds to the formation of a complex between a Li^+ cation and a C≡N group of PAN. However, this interaction is far weaker than the interaction between Li^+ and the C=O group of plasticizers (peak at 903 cm^{-1}).[81–83]

To interpret the experimental data on the dielectric permittivity, ionic conductivity and thermal properties of the PAN–EC–PC–$LiN(CF_3SO_2)_2$ system, a model was proposed,[84] which is illustrated in Fig. 4 as follows: a cell formed by polymer chains and containing 'free' EC–PC molecules, ion pairs and aggregates. All 'free' Li^+ ions are solvated by EC–PC molecules and C≡N groups so that the ion transport proceeds in the vicinity of PAN chains.

Min *et al.*[85] have synthesized a PAN membrane by phase inversion method initiated by the NIPS mechanism, *i.e.*, *via* the substitution of a nonsolvent for the solvent. DMF served as the PAN solvent and deionized water served as its nonsolvent. The PAN solution on a glass support was placed into a settling bath. Water penetrated into the polymer and displaced DMF. The ready membrane was vacuum dried for 24 h at 80 °C. For activation, liquid elecrtolytes, namely, 1 M $LiClO_4$ in EC–DMC, 1 M $LiPF_6$ in EC–DMC and 1 M $LiBF_4$ in EC–DMC (1 : 1 by volume), were used. The PAN membranes had large voids and cavities to be filled with liquid electrolytes upon gel formation (Fig. 5).

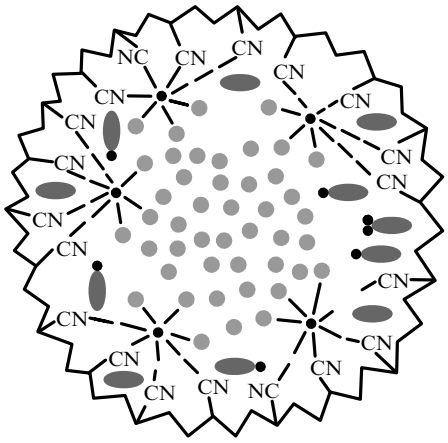


Figure 4. Model of the PAN–EC–PC–$LiN(CF_3SO_2)_2$ system.[84]

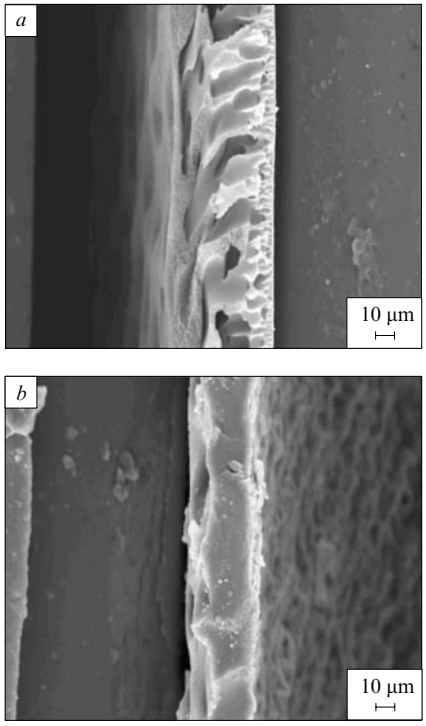


Figure 5. Scanning electron micrographs of chips of a porous PAN membrane (*a*) and a PAN-based polymer gel electrolyte (*b*).[85]

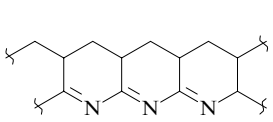
The electrochemical properties of polymer gel electrolytes were studied by impedance spectroscopy and linear voltammetry in symmetrical cells with stainless-steel electrodes. The gel electrolyte containing 1 M $LiPF_6$ in EC–DMC exhibited the highest ionic conductivity among the systems studied throughout the entire temperature range, 2.8×10^{-3} at 25 °C and 6×10^{-4} S cm^{-1} at −20 °C. All polymer gel electrolyte compositions were electrochemically stable up to 5 V (*vs.* Li/Li^+).

In the above study,[85] a membrane with the non-uniform porous structure was formed. On the other hand, Subrama-

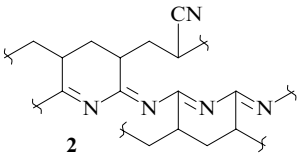
nia *et al.*[86] proposed to extract one of the components of the mixed polymer matrices in order to prepare microporous PAN membranes. The PAN–PVC mixture was prepared by dissolving polymers in DMF at 60 °C. From this viscous solution, a film was formed and then soaked in THF, which resulted in dissolution of PVC and formation of a porous structure. In the final stage, the ready membrane was placed in a 1 M $LiClO_4$ solution in EC–DEC (1 : 1 by volume). For the polymer gel electrolytes based on PAN–PVC in the 1 : 1 and 9 : 1 weight ratios, the maximum (5.0×10^{-3} S cm^{-1}) and the minimum (4.2×10^{-3} S cm^{-1}) conductivity values at 25 °C were determined. The addition of a larger amount of PVC induced the formation of a larger number of pores after its removal. The $\log\sigma$ *vs.* $1000/T$ dependence was linear and obeyed the Arrhenius equation. Due to the presence of a well developed system of interconnected pores, the gel electrolyte exhibited good transport properties (the Li^+ transport number was 0.62).

Choi *et al.*[87] prepared a PAN membrane by electrospinning and then soaked it with a 1 M solution of $LiPF_6$ in the following mixed solvents: EC–DMC (2 : 1 by weight), EC–DMC (1 : 1 by weight), EC–EMC (1 : 1 by weight), EC–DEC (1 : 1 by weight) and EC–DMC–DEC (1 : 1 : 1 by weight). The ionic conductivity of all polymer gel electrolyte compositions at 20 °C exceeded 1.0×10^{-3} S cm^{-1}, decreasing in the following series of 1 M $LiPF_6$ solutions in EC–DMC–DEC (1 : 1 : 1) > EC–DMC (1 : 1) > EC–EMC (1 : 1) > EC–DEC (1 : 1) > EC–DMC (2 : 1). Thus, a higher EC content leads to lower conductivity, because the transport of Li^+ ions is hindered due to crystallization of this solvent and increased solution viscosity.

Heating PAN to 100–200 °C results in the intramolecular interaction of nitrile groups to form 'ladder' polymer **1**. Simultaneously, an intermolecular reaction proceeds to afford cross-linked structures **2**.[88]



1



2

By heating the polymer solution, one can obtain less branched systems consisting of more extended blocks of conjugates bonds.

Akashi *et al.*[89,90] studied the PAN–$LiPF_6$–EC–PC and PAN–$LiPF_6$–EC–PC–GBL systems. Gel electrolyte films were prepared by casting from solution. All components were mixed, the resulting viscous solution was placed on a metal plate preheated to 110 °C and then cooled. Uniform flexible films were obtained. The ionic conductivity of all systems at room temperature exceeded 10^{-3} S cm^{-1}. Furthermore, the gel electrolyte solution was used for impregnation of cathodes, anodes and separators on assembling the $LiNi_{0.8}Co_{0.2}O_2$/C model cells. Heating the ready samples to 40 °C induced cross-linking of PAN to form gel electrolyte films on the electrode surface. All these factors contributed to a good contact between electrodes and the electrolyte and, correspondingly, to high efficiency of the cell. The retained discharge capacity was up to 93.9% after 100 cycles and 85.2% after 400 cycles.

Gel electrolytes based on PAN, $LiClO_4$ and PC with crown ether additives were synthesized.[91] Films were obtained by pressing the rubber-like mass prepared by heating the mixture of original component to 150 °C. The electrochemical properties were studied by impedance spectroscopy. It was found that the introduction of 15-crown-5- and benzo-15-crown-5-ethers favours the increase in the ionic conductivity of the gel electrolyte and the decrease in the charge-transfer resistance at the interface with the Li electrode. The conductivity of the polymer gel electrolyte of the composition (wt %): 8.5 PAN–3 $LiClO_4$–81 PC–7.5 (15-crown-5-ether) reached 6.3×10^{-3} S cm^{-1} at 20 °C.

Gel electrolytes based on PAN, lithium salts and various plasticizers exhibit the high ionic conductivity at room temperature ($\sim 10^{-3}$ S cm^{-1}), electrochemical stability up to 4.5 V (*vs.* Li/Li^+) and high transport numbers with respect to Li^+ (~ 0.6). Such characteristics allow these gel electrolytes to be used in lithium polymer batteries. Furthermore, PAN is a sufficiently fire-resistant material, which ensures the safety of the electrolytic system as a whole.[92]

Polyacrylonitrile is an amorphous polymer crystallized at a low temperature. It is poorly soluble in low-boiling-point and volatile solvents, which entails complications during preparation of gel electrolytes. However, the properties of polymer matrices can be changed by modification.

Rajendran *et al.*[93,94] used PVC as the polymer additive. Gel electrolytes were prepared by taking PC and $LiClO_4$ in different concentrations. The maximum conductivity of 10^{-3} S cm^{-1} at room temperature was demonstrated by the following composition (wt %): 24 PAN–6 PVC–8 $LiClO_4$–62 PC.

The main method of PAN modification is acrylonitrile co- and terpolymerization with different monomers to produce co- and terpolymers containing >70% of acrylonitrile. This can increase the solubility, decrease the viscosity and make films less brittle.[95,96]

By the emulsion polymerization, the P(AN-VA) copolymer of acrylonitrile (AN) and vinyl acetate (VA) was synthesized.[97] The P(AN-VA) membranes were prepared by the phase inversion method and then impregnated in a PMMA solution (3 wt %) in DMF and DEC to form a new kind of matrix. For activation, a 1 M $LiPF_6$ solution in EC–DMC–DEC (1 : 1 : 1 by volume) was used. A gel electrolyte based on P(AN-VA)–PMMA with the AN : VA molar ratio of 7 : 3 demonstrated the maximum ionic conductivity (1.88×10^{-3} S cm^{-1}) at room temperature and was electrochemically stable up to 5.2 V (*vs.* Li/Li^+). After 50 charge–discharge cycles, the Li/polymer gel electrolyte/$LiCoO_2$ cell retained up to 90% of its initial discharge capacity.

Liang *et al.*[98] synthesized several block copolymers of acrylonitrile with poly(ethylene glycol) [P(AN-PEG)]. They used PEG with different molecular masses (1000, 4000 and 10 000). The ready polymer, $LiClO_4$ and PC were mixed at 90 °C. The ionic conductivity and mechanical stability of samples increased with the increase in the number of $-C-O-C-$ units in PEG. Thus, the conductivity of the P(AN-$PEG_{10\,000}$)–$LiClO_4$–PC system was 1.45×10^{-3} S cm^{-1} at 30 °C and its Young's modulus was 0.18 MPa. These parameters are higher as compared with conventional PAN. In the plasticized block-copolymer, lithium ions interacted not only with C=O and C≡N groups but also with C–O–C. The fast segmental movements of the polymer chain widened the local free volume

and decreased the viscosity of substance within this volume. This favoured the increase in the ion mobility.

Thus, the polymer gel electrolytes based on PAN exhibit the electrochemical and mechanical properties sufficient for their successful application.

5. Gel electrolytes based on poly(vinyl chloride)

Poly(vinyl chloride) is a commercially available, chemically stable and poorly combustible low-crystalline polymer. It imparts mechanical rigidity to polymer gel electrolytes. Moreover, the presence of the lone electron pair of the chlorine atom in the polymer matrix chain favours the dissociation and solvation of lithium salts. Using X-ray powder diffraction and IR spectroscopy, the existence of a complex between PVC and Li^+ was evidenced. The diffraction patterns of pure PVC demonstrate two peaks at $2\theta = 9.36^\circ$ and 17.40°. The addition of a salt and a plasticizer shifts these peaks to 9.76° and 18.50°, respectively.[99] The presence of absorption bands at 1250, 928 and 892 cm^{-1} in the IR spectrum confirmed the formation of the PVC– Li^+ complex and its interaction with the plasticizer.[100]

Vickraman *et al.*[101,102] studied polymer gel electrolytes based on PVC, EC–PC and lithium salts ($LiClO_4$ and $LiCF_3SO_3$). These systems exhibit the conductivity of an order of magnitude of 10^{-6} S cm^{-1} at room temperature. Furthermore, their matrix was modified by the addition of PVDF-HFP. As was shown above, mixing of various polymer components has a beneficial effect on the electrochemical properties of gel electrolytes. However, in this particular case, a decrease in the ionic conductivity was observed so that its maximum value for all compositions was equal to 10^{-7} S cm^{-1} (25 °C). This can be associated with the poor compatibility of polymers and their inability to hold the liquid electrolyte.

Rajendran *et al.*[103] used pure PVC and PVC with the addition of PAN as the polymer matrices. The films were cast from a DMF solution. At 30 °C, the gel electrolyte containing (wt %) 30 PVC–8 $LiClO_4$–62 PC at 30 °C demonstrated a low ionic conductivity (6.7×10^{-6} S cm^{-1}); the conductivity of the 18 PBC–12 PAN–8 $LiClO_4$–62 PC (wt %) composition was an order of magnitude higher (3.2×10^{-5} S cm^{-1}). All gel electrolytes exhibited adequate mechanical and thermal stability.

Ramesh *et al.*[104,105] modified PVC with PMMA. A mixture of PVC–PMMA, $LiCF_3$ SO_3 and PC–DBF was dissolved in THF, stirred to produce a homogeneous solution and cast on a glass support. The ready films were studied by X-ray powder diffraction, thermogravimetry and electrochemical impedance measurements. The PVC–$LiCF_3SO_3$–PC–DBP system demonstrated the conductivity of 10^{-7} S cm^{-1} at room temperature. The addition of PMMA increased the conductivity to 2.0×10^{-4} S cm^{-1}. The mechanical properties of these gel electrolytes were also studied.[106] The films became less brittle after the introduction of PMMA. Thus, the Young's modulus was found to be 7.19 MPa for pure PVC and 6.05 MPa for the 70 PVC–30 PMMA (wt %) composition.

Mixing PVC with poly(ethyl methacrylate) (PEMA) also increased the ionic conductivity of gel electrolytes.[107,108] The films were prepared by casting from solutions in THF. As the liquid electrolyte, the $LiClO_4$ solutions in various plasticizers (EC, PC, DEC, GBL) were used. The temperature dependence of the ionic conductivity obeyed the Vogel–Tamman–Fulcher relationship. The maximum conductivity of 7×10^{-4} S cm^{-1} (30 °C) corresponded to a gel electrolyte of the 15 PVC–10 PEMA–8 $LiClO_4$–67 PC (wt %) composition. The conductivity increased with the increase in the ratio of the amorphous component (PEMA) in the mixture. In amorphous regions, the polymer chain segments are more mobile, which favours the transport of Li^+ ions within the chain and their hopping between chains. All the gel electrolytes exhibited good thermal stability up to 230 °C.

Tian *et al.*[109] used the PVC–poly(acrylonitrile-butyl acrylate) mixture [P(AN-BA)] for the preparation of a polymer membrane by the phase inversion method. A 1 M $LiPF_6$ solution in EC–DEC (1 : 1 by volume) was used for activation. The liquid electrolyte absorption was 380% with respect to the dry membrane mass. To complete the gel formation, the samples were heated at 80 °C in an inert atmosphere. The PVC–P(AN-BA) membrane represents a system comprising a PVC-enriched phase that provides the mechanical stability and a P(AN-BA)-enriched phase that serves as the conductivity channel. The gel electrolyte exhibited the tensile strength of 21 MPa, the ionic conductivity of an order of magnitude of 1.5×10^{-3} S cm^{-1} at room temperature and the electrochemical stability up to 4.5 V (*vs.* Li/Li^+).

Thus, gel electrolytes based on PVC possess a low ionic conductivity. The capacity of cells assembled with these electrolytes is substantially reduced on cycling, which can be attributed to the formation of a passivating LiCl layer on the anode surface.

6. Gel electrolytes based on polyacrylate systems

Besides the classical PMMA polymer matrix, various polyacrylate systems can be used in the preparation of gel electrolytes. Thus, gel electrolytes based on polyethylene glycol diacrylate, 2-ethylhexyl acrylate,[110] neopentyl glycol diacrylate,[111] lithium methacrylate,[112] butane-1,3-diol dimethacrylate (BDDA), ethylene glycol dimethacrylate,[113] copolymer of polyglycidyl diacrylate with polypyrrole,[114] copolymer of methacrylate with dimethylsiloxane[115] were described.

Polyacrylates are the polymers of acrylic acid esters with the general composition

$$\left(\mathrm{CH_2-\underset{\displaystyle \mathrm{CO_2R}}{\underset{|}{CH}}}\right)_n.$$

These polymers can be obtained from oligomers with a relatively low molecular mass. The polymerization of acrylates produces a three-dimensional network structure capable of holding liquid organic electrolytes. The chemically cross-linked polymer electrolytes based on polyacrylates are mechanically stable, have low glass transition temperatures and are compatible with liquid electrolytes. These properties predetermine their successful use in lithium batteries.[116,117] Polyacrylate systems are involved in preparation of homogeneous gels by thermally, UV and radiation-induced polymerization.

For instance, polymer gel electrolytes were prepared[118] by thermal polymerization of the butane-1,3-diol diacrylate monomer in a 1 M $LiPF_6$ solution in EC–EMC–DMC (1 : 1 : 1 by volume) in the presence of the AIBN initiator at 100 °C over a period of 1 h. The gel electrolyte containing

15 wt % of the polymer component exhibited the following conductivity:

T/°C	20	60	−30
σ/S cm^{-1}	3.2×10^{-3}	5.0×10^{-3}	5.6×10^{-4}

The $\log\sigma$ *vs.* $1000/T$ dependence was linear and obeyed the Arrhenius equation; this is why it was assumed that the conduction mechanism in the film is the same as in liquid electrolytes. As a result of polymerization, a three-dimensional structure was formed. The gel electrolyte film was characterized by good mechanical stability and the ability to hold liquid electrolytes. A C/$LiCoO_2$ cell was prepared with the use of a gel electrolyte precursor; the polymerization was carried out *in situ*. This system demonstrated good cyclability. Curves of the first charge–discharge cycle had a plateau at medium voltage of the charge (3.9 V) and discharge (3.7 V) branches (Fig. 6). The initial discharge capacity reached 780 mA h, the initial charge–discharge efficiency was 92.1%; after 300 cycles, the remaining capacity was >85%.

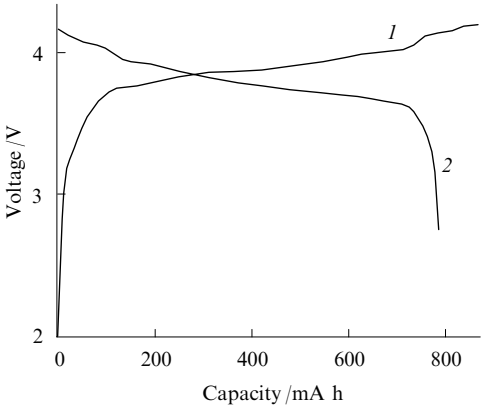
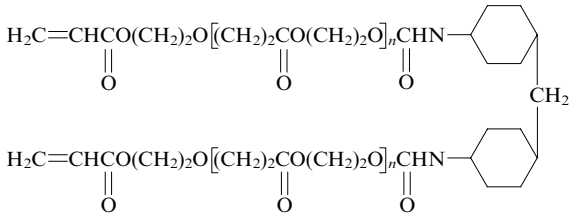


Figure 6. Curves of the first charge (*1*)–discharge (*2*) cycles for a C/BDDA–1 M $LiPF_6$–EC–EMC–DMC/$LiCoO_2$ cell.[118]

Kim *et al.*[119] used a cell with a $LiCoO_2$ cathode, a graphite anode and a gel electrolyte containing 5 vol % tetraethylene glycol diacrylate, 95 vol % 1.1 M $LiPF_6$ solution in EC–PC–EMC–DEC [30 : 20 : 30 : 20 (wt %)]. The thermal polymerization was carried out at 80 °C for 40 min in the presence of BP. The ionic conductivity of the gel electrolyte was 6.34×10^{-3} S cm^{-1} at 20 °C, the electrochemical stability was observed up to 4.5 V (*vs.* Li/Li$^+$). The performance characteristics of the cell were estimated at different temperatures. Thus, the discharge capacity at 20 °C was ~57 mA h for the current density of 0.5 mA cm^{-2} and the rate of 0.2 *C*. At the temperature of −10 °C, the capacity was ~42 mA h (81% of the discharge capacity at 20 °C). The use of EMC with a low freezing point (−55 °C) in a mixture with EC and PC improves the operation of cells at low temperatures.

Gel electrolytes based on poly(ether diacrylate) (PEDA), the reaction product of oligo(hydroxyethyl acrylate) with 4,4′-dicyclohexylmethane diisocyanate, and a 1 M $LiClO_4$ solution in either GBL or binary mixtures EC–PC, EC–GBL, PC–GBL (1 : 1 by weight) were studied.[120,121] At the ends of the PEDA chain, double C=C bonds are present which can open to form a network polymer capable of adequately holding liquid electrolytes.



Homogeneous transparent gel electrolyte films with the high ionic conductivity were obtained. The differential scanning calorimetry and impedance spectroscopy studies revealed their optimal characteristics which corresponded to a gel containing 20 wt % PEDA–80 wt % 1 M $LiClO_4$ solution in PC–GBL (1 : 1 by weight) with the conductivity of $(1.0-3.5)\times10^{-3}$ S cm^{-1} in the temperature range from −18 to 40 °C.[122]

The electrochemical properties of thin-film gel electrolytes based on PEDA and 1 M $LiBF_4$ solution in GBL, supported by either a fibre-like polypropylene separator or a microporous polypropylene PORP film (the Russian analogue of Celgard®), were studied.[123] The best characteristics corresponded to gel electrolytes on the porous (80%) nonwoven felt separator. The Li/gel electrolyte/CF_x primary cells which offer promise for the use in electrical cardiacstimulators were tested.

Using the thermal polymerization (with PB as the initiator), Kim *et al.*[124] synthesized a gel electrolyte which included an oligourethane acrylate as the monomer, triethylene glycole dimethacrylate as the modifying additive and 1 M $LiPF_6$ solution in EC–DEC (1 : 1 by volume) as the liquid electrolyte. The conductivity of this system was 4.5×10^{-3} S cm^{-1} at 20 °C, the electrochemical stability was observed up to 4.8 V (*vs.* Li/Li$^+$). This gel electrolyte was used to assemble the C/$LiCoO_2$ cells and the latter were tested at the voltage of 4.2 and 3.0 V, *i.e.*, the upper and lower limits, respectively. For the current density of 0.5 mA cm^{-2} (rate 0.2 *C*), the specific discharge capacity of such cell was 147 mA h g^{-1} relative to the cathode material mass. The capacitance decreased by ~20% after 40 cycles, which was associated with the loss of contact between the electrodes and the gel electrolyte and also with the gradual increase in cell internal resistance.

Wang *et al.*[125] studied gel electrolytes based on poly(acrylate-imide). The macromonomers of poly(ethylene glycol methyl methacrylates) (PEGMMA) with $M_n = 745$ and 1100 were dissolved in a 1 M $LiPF_6$ solution in EC–PC–DEC (3 : 2 : 5 by volume). Bis-maleimide (BMI) was added as the cross-linking agent. The polymerization was carried out at 90 °C for 1 h in the presence of AIBN. The resulting three-dimensional network could hold liquid organic electrolytes. The gel electrolyte based on $PEGMMA_{1100}$–BMI exhibited a high ionic conductivity (4.8×10^{-3} S cm^{-1} at 25 °C), the electrochemical stability up to 4.2 V (*vs.* Li/Li$^+$) and the Li$^+$ transport number of 0.29. After 100 cycles, the 95% of the C/gel electrolyte/$LiCoO_2$ cell capacity was retained.

The atom-transfer radical polymerization was proposed[126] as a method for synthesizing gel electrolytes, inasmuch as it proceeds at room temperature, which reduces the risk of gas formation in the cell. As the polymer matrix, PEGMMA ($M_w \approx 475$) and PEGDMA ($M_w \approx 330$) were

used; as the polymerization initiators CuBr, 2-bromo-2-methylpropionate (BMP), *N*,*N*,*N*′,*N*″,*N*‴-pentamethyldiethylenetriamine (PMDETA) were taken. The methacrylates : CuBr : BMP : PMDETA molar ratio was 100 : 1 : 2 : 1. The polymerization was carried out for 24 h in a 1 M $LiPF_6$ solution in EC – PC – EDC (3 : 2 : 5 by volume) as the reaction medium. The effect of different amounts of the PEGDMA cross-linking agent was studied. The PEGMMA : PEGDMA ratio of 80 : 20 proved to be the optimal. For the addition of 30 wt % of PEGMMA – PEGDMA copolymer, the highest conductivity of 2.1×10^{-3} S cm^{-1} was observed at 30 °C; in the interval from 40 wt % to 90 wt % of the added polymer , the conductivity varied from 1.7×10^{-3} to 3.7×10^{-6} S cm^{-1}. However, for 30 wt %, due to the insufficiently developed polymer network, the gel electrolyte represented a viscous liquid and the film could be formed only after 40 wt %. For a gel electrolyte containing 40 wt % PEGMMA – PEGDMA (80 : 20) wt % – 60 wt % 1 M $LiPF_6$ solution in EC – PC – DEC, the Li^+ transport number was 0.32, and the electrochemical window was 5.5 V.

The oligourethane dimethacrylate (OUM) and polypropylene glycol monomethacrylate (PGMM) composition, which was polymerized at double bonds upon the photo or thermal initiation in the liquid electrolyte medium, was used as the polymer matrix for gel electrolytes.[127–131] The conductivity of gel electrolytes containing 1 M $LiClO_4$ in GBL, 1 M $LiBF_4$ in GBL, 1 M $LiPF_6$ in EC – DMC (1 : 1 by volume) or 0.5 M $LiClO_4$ in PC – dimethoxyethane (1 : 1 by volume) at 20 °C exceeded 10^{-3} S cm^{-1}.

Song *et al.*[132] prepared gel electrolytes based on the mixture of PVDF-HFP and poly(ethylene glycol) diacrylate (PEGDA) in the 1 : 1 ratio. The polymer and the oligomer were mixed with a 1 M $LiPF_6$ solution in EC – DMC (1 : 1 by volume) and then a photoinitiator (2-chlorobenzophenone) and a curing agent (triethylamine) were added. As the result of UV polymerization, a three-dimensional network structure was formed. The microscopic analysis has shown that the pore size in gel electrolyte films formed from the PEGDA – PVDF-HFP mixture was intermediate between the pore sizes in compact PEGDA and the highly porous PVDF-HFP copolymer. In the gel electrolyte structure, the PVDF-HFP chains are randomly intertwined with the PEGDA network. As compared with individual PEGDA, the films based on the PEGDA – PVDF mixture have the higher mechanical stability and, as opposed to the highly porous PVDF-HFP copolymer, can hold the liquid electrolyte for longer periods. At room temperature, the ionic conductivity of the gel electrolyte was 4×10^{-3} S cm^{-1}. The C/PEGDA – PVDF (1 : 1) – 1 M $LiPF_6$ solution in the EC – DMC (1 : 1)/$LiCoO_2$ cell could be adequately cycled in the voltage range of 3.0 – 4.2 V. At 0 and −10 °C, the system retained 92% and 76% of the discharge capacity as compared with its value at room temperature.

Reiter *et al.*[133,134] used the UV-induced polymerization to prepare gel electrolytes based on PEMA and poly(2-ethoxyethyl methacrylate) (PEOEMA), which contained a $LiClO_4$ solution in PC. These electrolytes exhibited the ionic conductivity of up to 1×10^{-3} S cm^{-1} (20 °C), electrochemical stability up to 5.1 V (*vs.* Li/Li^+) and good mechanical properties. All the systems studied retained acceptable conductivity and good mechanical properties up to −20 °C.

III. Gel electrolytes with ionic liquids

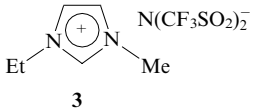
Owing to plasticizers they contain (EC, PC, DMC, DEC, *etc.*), the polymer gel electrolytes are characterized by the higher ionic conductivity as compared with solid polymer electrolytes. The liquid organic electrolyte is confined by the polymer matrix; however, for volatile solvents, the problems of flammability and electrochemical instability (particularly, at elevated temperatures) exist, which limit the scope of applicability of the corresponding devices.

Recently, ionic liquids, *i.e.*, melts of organic salts that exist in the liquid state in a wide temperature range, were proposed as an alternative to conventional solvents. As a rule, ionic liquids comprise a bulky organic cation and an inorganic or organic anion. Their asymmetrical structure and spatially separated charges prevent the organization of their crystal structure and determine the ionic (in contrast to molecular) nature of the liquid phase, which is responsible for their peculiar physicochemical properties: low melting point and virtually total absence of saturated vapour pressure, incombustibility, the ability to dissolve many compounds, high polarity and conductivity (1 – 18 S cm^{-1} at 20 °C) and also the wide electrochemical window (up to 6 V). Moreover, ionic liquids are nontoxic and pertain to the so-called green solvents. The properties of ionic liquids can be regulated by varying the nature of constituent ions. Naturally, ionic liquids are attractive for the use in many fields of science and technology, especially, in electrochemistry.[135]

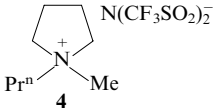
Ionic liquids are known since 1888; however, their extensive studies began only in 1992, when the use of 1-methyl-3-ethylimidazolium salts for lithium cells was reported.[136,137] In 2002, somewhat over 500 studies on this subject were published, while in 2006, the number of publications reached nearly 2000.[138,139]

Table 2 shows the characteristics of certain polymer gel electrolytes based on ionic liquids.

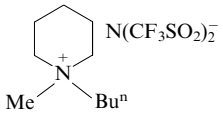
In recent studies, the ionic liquids with imidazolium (**3**),[149–151] pyrrolidinium,[152,153] piperidinium (**5**),[154] quaternary ammonium (**6**)[155] cations and $N(CF_3SO_2)_2^-$ anions were used for swelling polymer gel electrolytes. Susan *et al.*[156] have proposed a new conceptual name for these systems: 'ionic gels'.



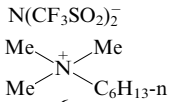
3



4



5



6

When polymer gel electrolytes are used with ionic liquids as the solvents, the Coulombic efficiency of the charge – discharge processes of $Li/LiCoO_2$ cells approaches 100%. The majority of ionic liquids are well compatible with the lithium anode and, in some cases, capable of forming protective SEI layers on its surface. For suppression of electrolyte decomposition, different additives can be used.[157,158]

Table 2. Ionic conductivity (σ) and the electrochemical window (U) of certain gel electrolytes with ionic liquids as the solvents.

Ionic gels	σ /S cm^{-1}	T /°C	U /V	Ref.
$P(EO)_{20}-LiN(CF_3SO_2)_2-BMI\text{-}N(CF_3SO_2)_2$	3.2×10^{-4}	25	5.60	140
$P(EO)_{20}-LiN(CF_3SO_2)_2-MPP\text{-}N(CF_3SO_2)_2$	2.8×10^{-4}	20	6.20	141
$PVDF\text{-}HFP-LiN(C_2F_5SO_2)_2-EMI\text{-}N(C_2F_5SO_2)_2$	$\sim10^{-3}$	25	5.50	142
$PVDF\text{-}HFP-LiPF_6-EMI\text{-}PF_6$	1.6×10^{-3}	20	5.00	143
$PVDF\text{-}HFP-Li(CF_3SO_3)-DMOI\text{-}CF_3SO_2$	3.2×10^{-5}	20	5.00	144
$PVDF\text{-}HFP-LiN(CF_3SO_2)_2-MPP\text{-}N(CF_3SO_2)_2$	0.3×10^{-3}	20	5.75	145
$PVDF\text{-}HFP-LiN(CF_3SO_2)_2-BEP\text{-}N(CF_3SO_2)_2$	$\sim10^{-4}$	20	5.50	146
$PEOEMA-LiPF_6-BMI\text{-}PF_6$	0.9×10^{-3}	25	4.30	147
$PEO\text{-}PMMA-LiN(CF_3SO_2)_2-TMHA\text{-}LiN(CF_3SO_2)_2$	$\sim10^{-5}$	20	–	148

Note. The following abbreviations are used: BMI is 1-butyl-3-methylimidazolium; MMP is *N*-methyl-*N*-propylpyrrolidinium; EMI is 1-methyl-3-ethylimidazolium; DMOI is 2,3-dimethyl-1-octylimidazolium; BEP is *N*-butyl-*N*-ethylpiperidinium; TMHA is *N*,*N*,*N*-trimethyl-*N*-hexylammonium.

Ionic liquids are promising solvents for lithium-ion batteries; however, their use is so far limited by the complications associated with their purification.

IV. Conclusion

In the modern literature, the gel electrolytes based on the most abundant polymers (PEO, PVDF, PVDF-HFP, PMMA, PAN, PVC, polyacrylates), lithium salts [$LiPF_6$, $LiClO_4$, $LiBF_4$, $LiN(CF_3SO_2)_2$] and organic solvents (EC, PC, DMC, EMC, DEC) are represented most widely. The active search for new polymer components and electrolytes is being carried out; however, the ideal system was not found so far. The development of portable electronic devices and also of electric vehicles to ultimately replace the internal combustion engine cars requires further investigation. To be successfully used in practice, the polymer gel electrolytes should possess certain characteristics, namely, a high ionic conductivity, good mechanical properties, a wide electrochemical window and a large range of working temperatures. The components used in their preparation should be commercially available, which also concerns the lithium cell technology. A polymer gel electrolyte serves both as a separator and an electrolyte, preventing the dendrite growth and providing the SEI film formation.

In the field of development of lithium cells, the polymer gel electrolytes based on poly(vinylidene fluoride) and polyacrylates hold the greatest promise. Moreover, the recent extensive studies on modifying polymer matrices by copolymerization and cross-linking were aimed at the decrease in their degree of crystallinity and, hence, the increase in the polymer affinity for the organic solvent, which serves to hold larger amounts of liquid electrolytes. Thus, a copolymer of poly(vinylidene fluoride) with hexafluoropropylene combines the high mechanical stability (due to crystalline PVDF) and the ability to absorb electrolyte (due to HFP units). Gel electrolytes based on the PVDF-HFP copolymer prepared according to the Bellcore technology are widely used in manufacturing lithium cells. Polymers capable of forming network structures are good candidates for the use as matrices for homogeneous gels. Moreover, the ability to hold liquid electrolyte remains even at the minimum content of the polymer component. Network gel electrolytes can be obtained *in situ* by the radiation and thermal polymerization, which introduces only insignificant changes into the technology of lithium cells with liquid electrolytes.

Finally, it should be noted that the appearance of nanostructured electrode materials had a substantial effect on the development of lithium cells.[159, 160] Their new design involves the fabrication of thin electrode coatings as rods, columns or plates. This makes it possible, on the one hand, to increase the contact surface between the electrolyte and the electrode material and, on the other hand, shorten the time needed for the electrode process to proceed. Naturally, the use of nanotechnologies will mean the development of new types of gel electrolytes. Particularly, the role of additives that provide the transport of lithium ions without any direct contact with the organic electrolyte (*e.g.*, crown ethers) may increase.

Thus, the studies of polymer gel electrolytes aimed at improvement of characteristics of electrochemical systems are in progress and attract keen attention.

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