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The role of the solvent in PMMA gel polymer electrolytes

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Abstract: Ionic mobility and solvent vapor pressure were studied on gels containing sodium perchlorate, polymethylmethacrylate and sulfolane as a solvent. The excess of solvent increases markedly the mobility of ions and is indicated by solvent evaporation at elevated temperature. The solvent is bonded similarly as in the liquid solution of sodium salt. The heat of solvent evaporation from gels is near to that of pure solvents.

Keywords: Gel polymer electrolyte; TGA, NMR spectroscopy; conductivity; sodium polymer electrolyte

1 Introduction

Lithium-ion and lithium-polymer batteries are the most hopeful candidates as energy sources suitable for electric vehicles and electric traction in general. The mobility of lithium ions in them is surprisingly lower than the mobility of sodium ions and mobility of bulky anions. An important component in many of them is an electrolyte containing aprotic organic solvents and in the case of polymers also organic macromolecular substances. The stability of these substances at elevated temperature is quite essential from the viewpoint of their safety. This question is treated in this paper.

Sodium ion containing polymer electrolytes were used as the interaction of larger sodium ion with the polar groups in the polymer is expected to be smaller, this resulting in higher expected ionic mobility.

Gel polymer electrolytes have been studied in our laboratories for more than two decades [1]. Many papers have been published by electrochemists concerning polymeric electrolytes [2]. Recently, polymer electrolytes for lithium batteries have attracted attention not only as important materials for lithium batteries. The conductivity and ionic movement in them has been a subject of intensive interest for example on meetings [3], where many electrochemists reported both experimental data and computations of cation movement obtained by methods of molecular dynamics. The presence of another component – the solvent for lithium ions – is taken to account quite seldom. The aim of this paper is to show on the role of solvent in gel polymer electrolytes which contain sodium cations.

It is known that lithium ions are bonded to the chains of macromolecules thanks to their small ionic radius and their affinity to polar groups present on polymer chains. Therefore we decided to introduce sodium salts in the case of which the chemical or quasichemical bonding with the polymeric chains would be emphasized to much lower extent. For the same reason, we have wanted to use a solvent which is not so common and we have chosen sulfolane as solvent component in the gels. Nuclear magnetic resonance (NMR) spectroscopy has been used to study polymer electrolytes. Most studies of polymer electrolytes have investigated the temperature of sub-ambient glass transition, with amorphous polymer systems with alkali metal salts as the conducting species. In these systems, ion transport has mostly been associated with the segmental motion of the polymer as significant conductivity is only observed above the glass transition temperature of the system. Cation mobility is of particular interest in these systems with regard to polymer-based batteries [4].

Cation mobility in polymer electrolytes was previously investigated by measuring the line width of solid-state nuclear magnetic resonance (NMR) spectra [5, 6]. The spectral line widths are a result of internuclear dipole-dipole interactions. When the nuclei are fixed, interactions are

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accentuated, which results in a broad line width commonly referred to as the rigid lattice linewidth. As the mobility of the cation increases, the NMR linewidth decreases due to the averaging of the interactions experienced by each nucleus.

Lopes *et al.* [7] presented conductivity and ^{1}H and ^{7}Li NMR spin-lattice relaxation measurements as a function of temperature in a series of polymer electrolytes formed by amylopectin-rich starch plasticized with glycerol and containing $LiClO_4$. The electrical characterization was carried out using impedance spectroscopy. From electrical and NMR measurements, characteristic dynamic parameters such as activation energies and motional correlation times were obtained.

Moreover, we have to study materials for lithium polymer batteries from the viewpoint of fire safety, so often discussed nowadays; we expect that addition of sulfolane will increase the flash point of the solvent and in this way also improve the safety of the batteries. We have succeeded to prepare gel polymer electrolytes from solutions of sodium perchlorate in sulfolane (SL) added to propylene carbonate (PC) (1:1 by volume) and used it for preparation of samples. The main idea was to use constant amount of salt and monomer and vary the amount of solvent. We have measured electric conductivity at room temperature, ionic mobility of sodium ions by NMR relaxation times T_2 (NMR relaxometry) and behavior at elevated temperatures by DTA – GRA method. We have studied the formation and properties of gel polymer electrolytes consisting of PMMA and alkali metal salt in aprotic solvent. In this paper, we report how excess of solvent changes the properties of PMMA – solvent gel electrolytes.

This manuscript is focused on the properties of substances useful for electrochemical systems. Several quantities are expressed according to practice common in electrochemistry. Mainly, we have used the concept of molar conductivity as the ratio between specific conductivity and concentration of proper compound. It is estimated for concentration in grams per liter and its value should be constant if no interactions between ions and surrounding exist. Similarly the enthalpy estimated by DTA is expressed in kJ/g (molar concentration instead). The aim of this paper is to show the role of solvent in gel polymer electrolytes.

2 Methods and Experiments

Changes in relaxation time measured by NMR, it is possible to characterize changes in ionic conductivity of the gel and its changes. In the electrolytes, relaxation times T_1 and T_2, were measured by means of NMR techniques. Any excited magnetic moment relaxes back to the equilibrium, the z axis. There are two components of this relaxation for isotropic systems in the absence of chemical exchange: the longitudinal or spin-lattice T_1 and the transverse or spin-spin T_2. In non-viscous liquids, the usual relation is $T_2 = T_1$. But some processes like scalar coupling with quadrupolar nuclei, chemical exchange, or interaction with a paramagnetic center can accelerate the T_2 relaxation in such a way that T_2 becomes shorter than T_1.

The relaxation of quadrupolar nuclei ($I > 1/2$) has been discussed by Abragam [8]. For a nucleus such as ^{23}Na with a nuclear spin of $I = 3/2$, in the limit of extreme narrowing, the spin-lattice relaxation time T_1 is given by

$$1/T_1(2\pi^2/5)(e^2qQ/h)^2\tau_c$$

where Q is the nuclear quadrupole moment, e^2q is the electric field gradient at the nucleus (assumed here to be cylindrically symmetric), and h is Planck's constant. The rate of rotational diffusion of the electric field gradient at the nucleus is expressed by correlation time (τ_c) for the orientation of the field gradient with respect to the applied magnetic field.

Molecules in liquids are in rapid motion with respect to the inverse Larmor frequency. The T_1 relaxation of an isolated spin pair is characterized by the correlation time (τ_c). Clearly the fastest motion possible is the free reorientation of a molecule, so that, depending on the type of motion, the cut-off frequency ω_c is anywhere between zero and 10^{13} Hz. The correlation time, diffusion, T_1 and T_2 relaxation depends on the internal chemical structure of molecules and internal coupling forces between the nuclei [9]. Changes in relaxation during the polymerization may be characteristic of the changes in the chemical structure of polymers and electrical conductivity of the gels. It is understandable that a change in polymerization may also affect the glass transition temperature T_g. The relaxation time of bound sodium is found to be $T_1 = 4.3$ ms, whereas for free sodium the time is determined at $T_1 = 57$ ms [10]. The spin-spin relaxation time T_2 can be measured using the spin echo method; alternatively, $T_2^\star$ can be calculated from the half-width of the spectral line. However, the line width for non-viscous liquids is most often dominated by field inhomogeneity. Fortunately, the dephasing of spins isochromats resulting from the field inhomogeneity is a reversible process; it can be refocused by using a 180 degree pulse inserted in the center of an evolution time. Parameter $T_2^\star$ is the time constant of dephasing, and it is caused by a combination of relaxation and magnetic inhomogeneity [10, 11].

A disadvantage of the spin-echo method is its lower sensitivity, because echo-time T_E may not be comparable to the short T_2 relaxation time. ^{23}Na nuclei give a very weak signal, which results in a very low signal-to-noise ratio and approximation that $T_2 = T_2^*$. The classical treatment of NMR relaxation and line width shows that the theoretical half of spectral line width Δf in a homogenous magnetic field can be expressed as $\Delta f = 1/(\pi \cdot T_2^*)$ where T_2^* is the effective spin-spin relaxation time which is affected by spin-spin interactions. The line width of a ^{23}Na NMR spectral line, measured by 1-pulse MR sequence, is therefore given by the interactions between the atoms (molecules) in a polymer sample or the molecular flexibility. A disadvantage of T_2^* calculation from the half-width of the spectral line is that although it provides a much better signal-to-noise ratio, the very large inhomogeneity of the basic magnetic field will expand the spectral lines and reduce T_2^*.

3 Chemicals

Solvents (PC and SL) were distilled in vacuum, monomer methylmethacrylate (MMA) was distilled at atmospheric pressure. $NaClO_4$ was dried in an oven at 180°C for 24 hours. Ethylene dimethacrylate (EDMA) and polymerization catalyst benzoin ethyl ether (BEE) were used as received (Sigma- Aldrich). The amount of $NaClO_4$ corresponded to 1 M with respect to MMA, which was kept approximately constant. Various amounts of solvent SL+PC and 0.16 g of EDMA as cross linking agent were added.

The polymerization was performed under UV illumination. Compositions of the samples are listed in Tab. 1. The samples with lower amount of solvent were almost rigid and they have turned to be jelly-like if the amount of solvent increased. The samples are described by the dilution, computed as reciprocal of concentration of salt in the electrolyte, not taking into account the volume of MMA in the reaction mixture before its polymerization.

Conductivity was measured between two metallic electrodes by means of a potentiostat BioLogic in EIS mode and by extrapolation to frequency ca. 10 kHz. All NMR measurements were performed on the 4.7 T / 200 mm MR system at the Institute of Scientific Instruments, Academy of Sciences of the Czech Republic. The resonance frequency of ^{1}H nuclei is 200 MHz, and the frequency of ^{23}Na is 51 MHz. DTA measurements were performed by SDT Q600 V20.9 instrument. This device is equipped with an IR spectroscopic analyzer of released gases.

Table 1: Compositions of the samples.

sample	dilution ml/mol	τ_2 ms	γ S/cm	Λ S/(mol/ml)
1AS	227.70	0.31	$1.84 \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$
2AS	238.79	0.31	$1.78 \cdot 10^{-3}$	$1.94 \cdot 10^{-3}$
3AS	250.00	0.31	$1.73 \cdot 10^{-3}$	$2.12 \cdot 10^{-3}$
4AS	261.19	0.30	$9.33 \cdot 10^{-4}$	$1.27 \cdot 10^{-3}$
5AS	272.83	0.27	$1.05 \cdot 10^{-3}$	$1.57 \cdot 10^{-3}$
6AS	284.22	0.47	$6.22 \cdot 10^{-2}$	$1.02 \cdot 10^{-1}$
7AS	295.18	0.54	$7.14 \cdot 10^{-1}$	$1.26 \cdot 10^{0}$
8AS	308.56	0.69	$9.95 \cdot 10^{-1}$	$1.90 \cdot 10^{0}$
5BS	liquid	2.43	-	-

4 Results

The relaxation time T_2 (in ms) of sodium ions in the gel changes in the process of gel polymerization from values typical for ions in solutions to values markedly lower [13]. Apparently the values of T_2 decrease from fairly high ones to values indicating limited mobility of the ions (see Fig. 1). On other words, it increases if the dilution by solvent increases from rather low values to a constant.

The values of ionic conductivities are plotted in the same Fig. 1. We see that both values –conductivity and relaxation time – start to increase markedly for dilution higher than 270 ml/mole approximately. Note that the conductivity is expressed as molar quantity, which is evaluated as the ratio of specific conductivity (S/cm) to molar concentration (mole/dm^3) as it is used in electrochemical science, and plotted in a logarithmic scale. The data are summarized in Table 1 together with the composition of the samples.

The DTA-GTA curve of a gel SA-5 as a typical example is plotted in Fig. 2. The initial heat flow up to temperatures 150–200°C is endothermic. Therefore it was easy to integrate the heat flow to the point at which the heat flow changes sign towards a positive one. In Figs. 3 and 4, the analysis of gases formed by DTA measurement is plotted. These figures are a direct output from the DTA device. Their graphic quality is difficult to change therefore. The results are ordered in ascending order from SA1 to SA8 (see tables). The magnitude of the signal is drawn on vertical axis for a series of selected wavenumbers and for temperature ascending to 600°C. The gases escaping from the samples due to heating are analyzed by IR spectroscopy. At lowest temperatures in the endothermic range, there is some formation of components with lowest characteristic frequencies and the gases are supposed to be formed from the re-

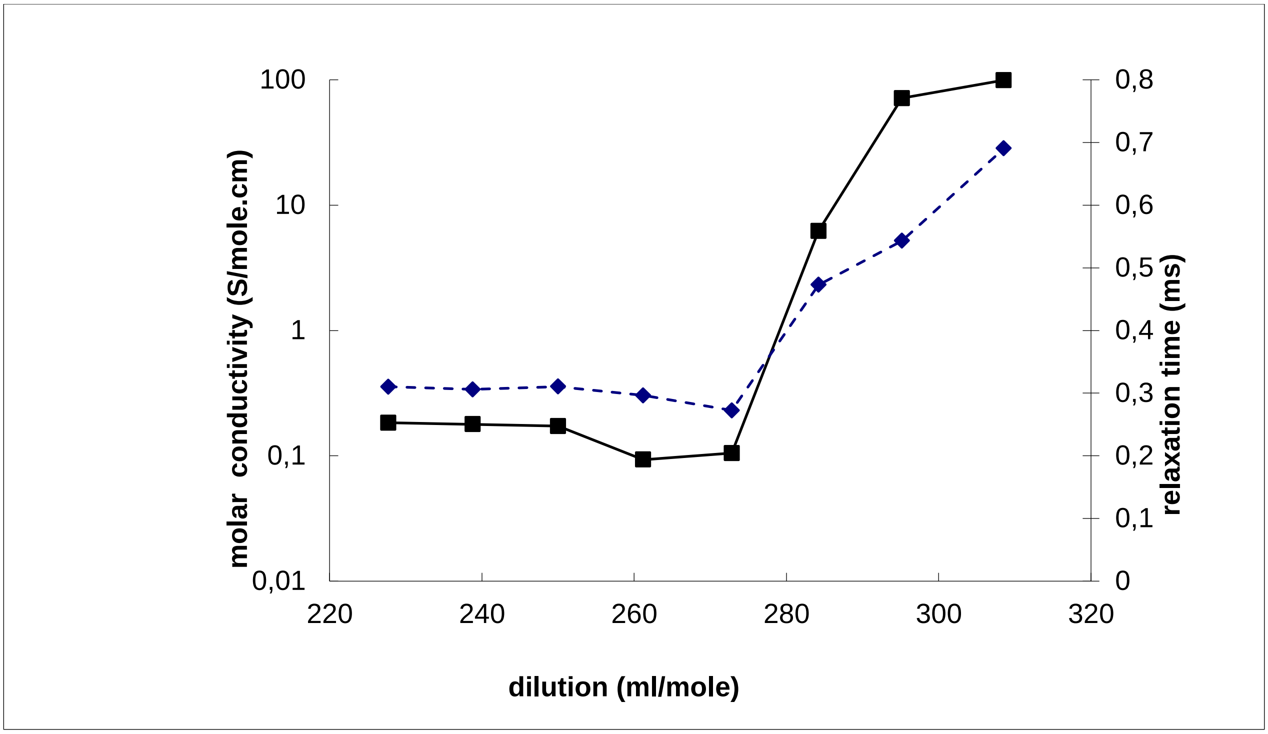

Figure 1: Relaxation time (broken line) and molar conductivity (solid line, logarithmic scale) plotted for various dilutions of the gel by propylene carbonate. Units are according to the usage in electrochemistry.

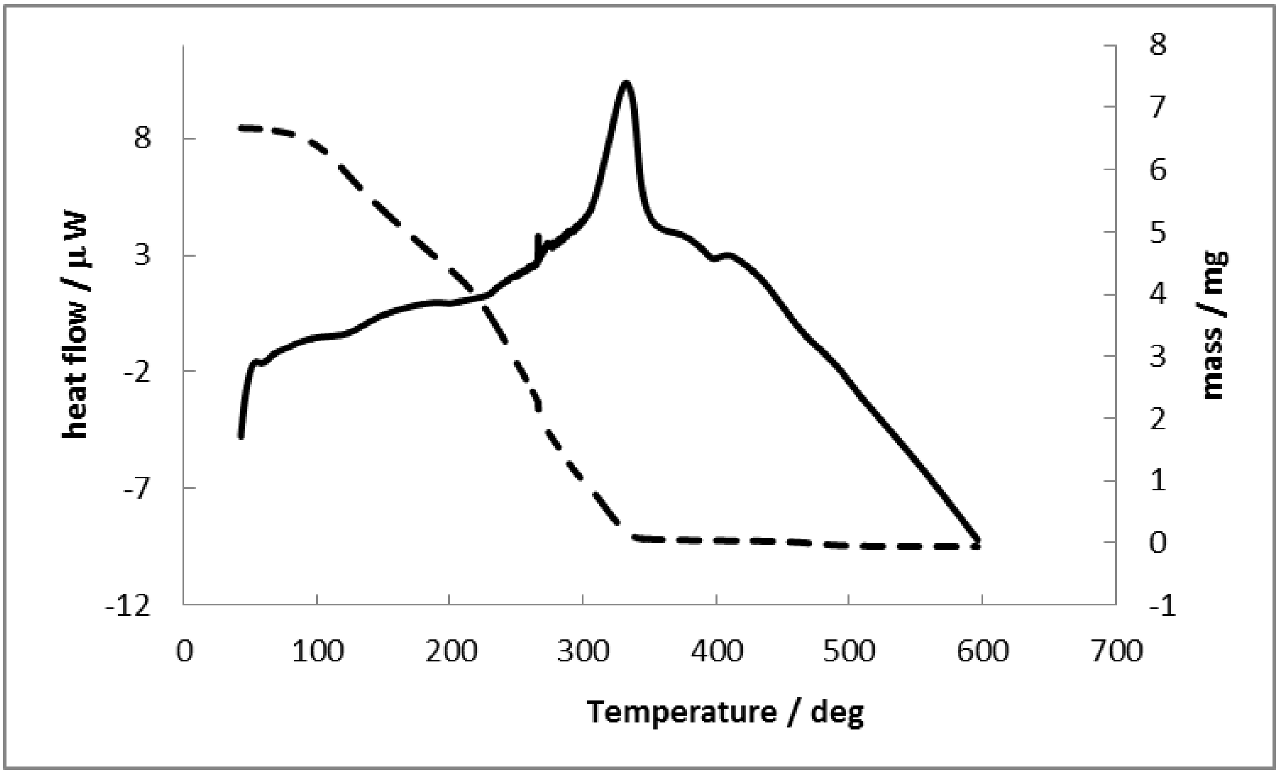

Figure 2: Example of a DTA – GTA curve. Full line: evolution of heat, broken line – mass loss.

dundant solvent (liquid) phase. It can be concluded that this is some evaporation of solvent from the gel, while the exothermic one corresponds to oxidative cleavage of polymeric components.

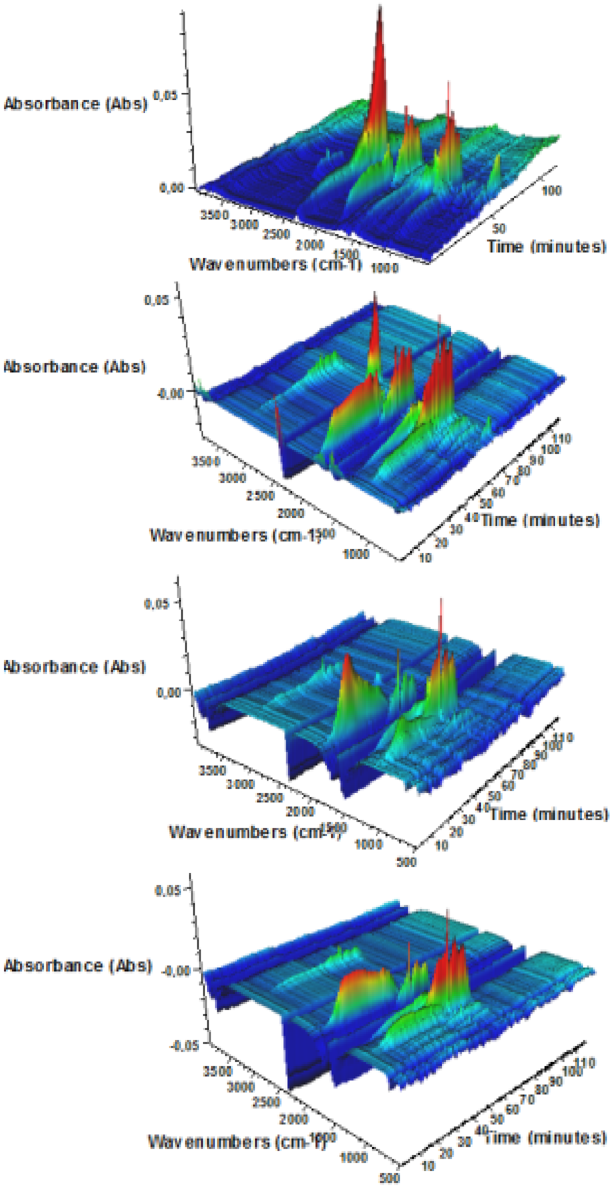

Figure 3: Decomposition of samples 1AS to AS5 monitored by IR spectroscopy (meaning of sample notification see Tab. 1).

Vertical axis: relative amplitudes of signals corresponding to wavenumbers of components detected by mass spectrometer, horizontal coordinates are wave numbers at which the outgoing gases were investigated and time of heating linearly from room temperature to 600°C. The signals obtained at lowest wavenumbers are supposed to correspond to evaporation of solvent.

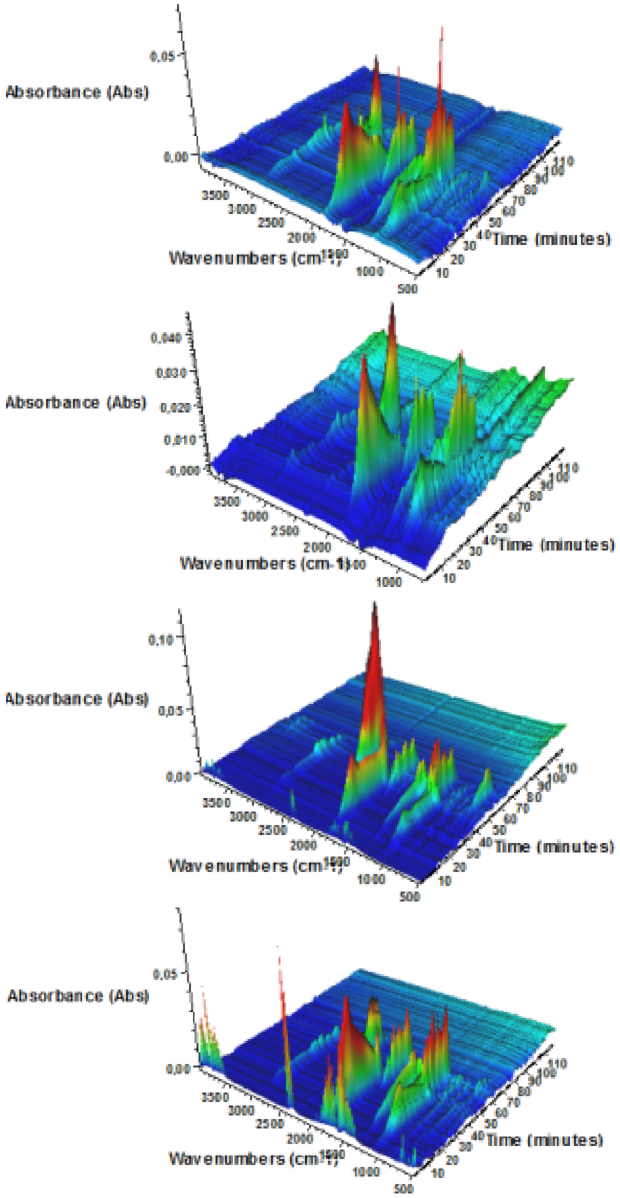

Figure 4: Decomposition of samples 5AS to 8AS monitored by IR spectroscopy (meaning of sample notification see Tab. 1).

The integrated heat uptake is listed in Tab. 2, where also the mass loss is recorded. Therefore it was easy to calculate specific heat of solvent evaporation. The values are between 350 to 400 J/g (see Tab. 2), a corresponding value for PC can be 510.5 J/g [14]. For the comparison, the heat of evaporation of pure SL is 556 J/g at room temperature [15, 16]. These two values are only in a qualitative agreement as the observed heat is lower. That may originate either from easier evaporation from the composite perhaps by the generation of some more volatile substance or by any other effect present in a three component system

Table 2: Explanation of columns: M of salt: amount of salt in the sample, dilution: – expressed as volume (cm^3) per 1 mole of solvent present in the sample, T cut-off: temperature at which evolved heat changes sign to endothermic reaction, cut-off mass is the mass at that point and Δm is the loss of mass at that point, Q is the heat flow, H_{total} is integrated energy output to cut-off point, ΔH_1 is the same related to 1 g of evaporated solvent.

sample	M of salt mole	dilution cm^3/mole	T cut-off	Initial mass mg	cut-off mass mg	Δm mg	q J$_{min}$	H_{total} J	ΔH_1 kJ/g
AS-1	0.0044	227.7	250.5	5.01	2.79	2.22	−80.60	$-1.34\cdot10^{0}$	$-6.05\cdot10^{-1}$
AS-2	0.0042	238.8	213.4	6.21	4.11	2.10	−37.49	$-6.25\cdot10^{-1}$	$-2.98\cdot10^{-1}$
AS-3	0.0040	250.0	207.4	5.75	4.02	1.73	−39.35	$-6.56\cdot10^{-1}$	$-3.80\cdot10^{-1}$
AS-4	0.0038	261.2	142.1	6.14	5.07	1.07	−24.67	$-4.11\cdot10^{-1}$	$-3.84\cdot10^{-1}$
AS-5	0.0037	272.8	135.2	6.67	5.65	1.02	−20.58	$-3.43\cdot10^{-1}$	$-3.37\cdot10^{-1}$
AS-6	0.0035	284.2	153.8	4.55	3.42	1.13	-39.11	$-6.52\cdot10^{-1}$	$-5.78\cdot10^{-1}$
AS-7	0.0034	295.2	167.8	6.76	5.27	1.50	−33.47	$-5.58\cdot10^{-1}$	$-3.73\cdot10^{-1}$
AS-8	0.0032	308.6	138.2	6.40	5.13	1.27	−24.18	$-4.03\cdot10^{-1}$	$-3.17\cdot10^{-1}$

(repulsion between polymer and solvent molecules of solvents and polymer).

5 Discussion

Following conclusions can be drawn from described results:

- The excess of solvent increases the specific conductivity and simultaneously the mobility detected by NMR measurements.
- Therefore, the movement of sodium ions is not so deeply hindered by any interactions with the polymeric chain. Partly, this is due to the properties of sodium ion in comparison to those of lithium. The influence of polymer – sodium ion interaction is much weaker and therefore not so important. The hopping process expected in sodium polymer electrolytes is less effective than the same in lithium system.
- Therefore, movement of sodium ions must occur in liquid phase dispersed in the polymer matrix. Then the movement of the ion is governed by an analogy of movement in liquids where the Stokes law controlled friction is substantial.
- Similar behavior has been described several times in other systems. For example, Reiter *et al.* [17] found that the presence of PC increased the conductivity of gels formed by MMA and ionic liquid more than by one order of magnitude.
- The results described in this paper can help to understand processes in lithium batteries at temperatures over 100°C which may result in the destruction of the battery.
- The rigidity and consistency of the gel electrolyte can be adapted very easily by the ratio between monomer and organic solvent used for their synthesis, on contrary to many references given on reinforced electrolytes – for example, given by [17].
- Appropriate rigidity of gel polymer electrolyte enables it to be used as a separator between the electrode and it will increase the fire safety of lithium – ion cells.

6 Conclusions

The aim of this paper was to indicate the role of solvent phase in the gel. It was concluded, that the increasing content of the solvent positively influences the conductivity and ionic mobility of sodium ions in the gel. The interaction between the cations and the polymeric molecules does not exercise any prevailing role.

First stage of heating is always connected to the emission of solvent to the surroundings. As the solvent is flammable, it may be one of the sources of possible incineration. Therefore, the ratio between solvent and polymer in these gels should be optimized carefully in order to obtain required mechanical rigidity of a self-supporting gel sheet suitable for assembling of lithium — ion cells.

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