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Properties of Electrolytes for Li – ion Batteries with Higher Fire Safety

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Abstract. In modern Li – ion batteries are used, as part of the electrolyte organic solvents, which are flammable. In this work we are investigate the influence of different solvents and their mixtures on the flashpoint due find a solvent with increase the safety of such battery. We are taking the flashpoint as main safety parameter. Other properties that we observed are the specific conductivity and permittivity with both are important for solvent classification as appropriate for electrolytes usability.
Another property for useable electrolytes is the melting point temperature and the temperature work window for lithium - ion batteries. In this paper it will be presented some properties of these mixtures from new solvents with commonly used solvents for aprotic electrolytes.

Key words

Aprotic electrolyte, Batteries, Specific conductivity, Fire safety, Permittivity.

1. Introduction

In most mobile devices are used Lithium – Ion batteries. Their advantage is the ratio of high capacity and small weight. Because of Lithium use it is not possible to use water as solvent even if it is cheap, available, nontoxic and it possess appropriate rheological properties. For lithium – ion batteries are used the aprotic liquid solvents or gels. Gel is in the fact a electrolyte bounded in appropriate polymer.[1]
There are two mine directions for the battery safety increasing. The first one is the electronic protect. This is in praxis performed by adding an integrated circuit with evaluated the temperature, charging and discharging current, voltage on the cell and in case of excess one of the criteria disconnects the damaged cell. This action stops the positive heat feedback and prevent from destroying the whole battery. The second way is to use a new less flammable or inflammable materials with can work in higher temperatures without destruction.

A. Solvents

Solvents are substances that allow to dissolve an another substance in it without a chemical reaction with the solvent. The dissolved substance can be again removed from the solvent without a chemical change of the solvent composition. The water is the most used solvent which has been paid a great attention in all fields dealing with this issue. Inorganic solvents were for a long time, regarded as typical aprotic solvents. In few past decades was a minor attention given to the organic aprotic solvents. A lot of solvents, especially doublepol aprotic solvents have appeared in new publications almost in connection with electrolytes and ions transfer.[2]
Correct selection of solvent, for individual applications depend on several factors among them the physical properties are the most important. The solvent should be liquid at temperature and pressure in with it is used. We have to take into mind the dynamic properties such viscosity, diffuse coefficient and temperature conductivity. Electric, optic and magnetic properties like dipole moment, relative permittivity, refractive index, magnetic and electric conductivity have impact on solvents behaviour. Even the molecular characteristics such as size and orientation of particles and relaxation time have effect on dissolve ability.[2]
Between solvents requirements for batteries applications include the temperature range for liquid state especially in low temperatures, low vapour pressure in the maximum work temperature for given application to explosion prevents, high relative permittivity, low viscosity and low molar mass for ensuring high ion mobility, chemical stability to the electrode material, availability, low cost, easy to clean and nontoxicity. The requested solvents properties for use in electrolytes can be divide into two main groups: electrical and physical. In table I are shown properties of used solvents.

Table I. Solvents properties

Solvent	Density [$\text{kg}\cdot\text{m}^3$]	Viscosity [$\text{mPa}\cdot\text{s}$]	Relative permittivity [-]	Melting point [°C]
Dimethyl sulfone	1450	1.14 (at 123°C)	48	110.0
Sulfolane	1261	10.07 (at 30°C)	44	27.5
Ethylene carbonate	1321	1.50 (at 40°C)	89	36.3
Propylene carbonate	1190	2.50 (at 25°C)	65	-55.0
Dimethyl sulfoxide	1096	1.96 (at 25°C)	47	18.6
Dimethyl carbonate	1071	0.75 (at 25°C)	2.8	-43.0

B. Electrical properties

The electric solvent response depends not only on electric field and molecular dipole moment also on influence of neighbour dipoles. The dipole moment is the degree of separation of the positive and negative charge in molecules and its unit is Debay. The solvents with high symmetric molecule can have the dipole moment on zero level, but some electronegative atom bounded to aromatic kernel causes a dipole moment. Some solvents are very polar with dipole moment around 4D ($1\text{D} = 3.33564\cdot10^{-30}\ \text{C}\cdot\text{m}$) or higher like glycerine, ethylene carbonate, propylene carbonate or sulfolane[2]. For batteries are used polare solvents. As a main electric property, with is observed is specific conductivity of electrolytes. The specific conductivity is measured by help of conductivity cell and impedance spectroscopy. The results are compared with reference sample (in our case $1\ \text{mol}\cdot\text{l}^{-1}$ KCl solution with specific conductivity at 25°C is $111.80\ \text{mS}\cdot\text{cm}^{-1}$). The second observed property is permittivity or dielectric constant. On all solvents used for electrolytes is posed high permittivity requirement minimal $\varepsilon_r > 30$ due the good cleavage of salt molecule to ions (the electrostatic force between salt atoms is due the solvent permittivity decreased on $\frac{1}{\varepsilon_r}$).[3]

C. Physical properties

From physical properties was the flash point observed. The flash point is the lowest temperature over calculated to the standard atmosphere pressure (equation 1) at with the vapour on the sample surface by applying the test flame are torched and burn less than two seconds and then spontaneously extinguishes.[4] The samples were measured be open cup method.

$$T_c = T_0 + 0.25\cdot(101.3 - p) \qquad (1)$$

where T_c is corrected temperature, T_0 is measured temperature at ambient pressure and p is the ambient pressure in kPa. Equation 1 applies exactly for pressure range from 98.0 kPa to 104.7 kPa.

Another required property is the dynamic viscosity. For easy ions motion it is necessary that the dynamic viscosity is as low as possible. Another property for electrolytes characterisation is the melting point. By comparison of saturated vapour tension above the blank solvent with saturated vapour tension above solution of non-volatile material in the same solvent is shown that vapour tension above solution is always lower then above a pure solvent. L. VON Babo (1848) examined this effect kvantitativ and discovered that the relative vapour tension (difference between the vapour tension of solvent and solution divided by vapour tension of solvent) decreases is independent on temperature. The vapour decreas on concentration study A. Wüllner (1856) and mathematically determined F. M. Fakult (1886). They find out, that the relative decreasing of vapour tension of solvent about solution is set by molar fraction dissolved matter in solution so-called Rault law. Decreasing the vapour tension about solution causes the bowling point increase and the melting point decrease. The degree of melting point lowering depends mainly on the solvent cryoscopy constant and that by equation 2.

$$-\Delta T_t = K_f \cdot b \qquad (2)$$

where $-\Delta T_t$ is the melting point decrise, K_f cryoscopic constant and b is the solution molality.

2. Experiment

The flash point measurement was made in indoor conditions. The measurement was made by open cup method and that by applying the test flame with specified diameter of 2 mm after two minutes of sample tempering. Each sample for this measurement has 2 ml volume. The samples were composed from two solvents (with changing solvents volume ratio) and in each sample was dissolved LiClO_4 salt in concentration of $1\ \text{mol}\cdot\text{l}^{-1}$. The salt was, before adding into sample, dried for 24 hours at 85 °C in vacuum oven.

The results are shown in figure 1. From curves can be seen that the highest flash point have ethylene carbonate with sulfolane. With increasing sulfolane ratio increases the flash point of all samples too.

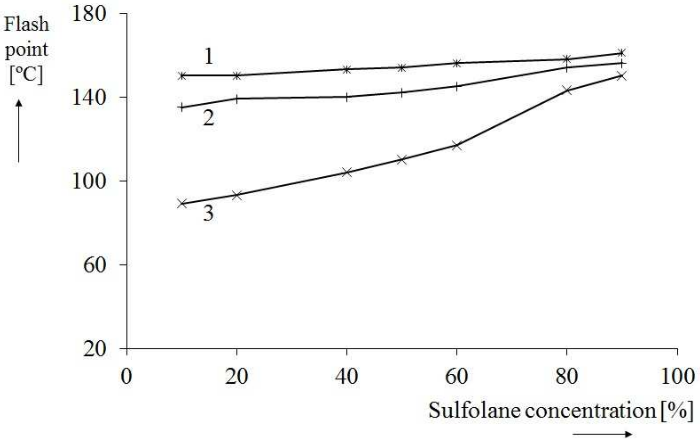

Fig. 1. The Flash point dependence on sulfolane concentration curve 1 Sulfolane + ethylene carbonate, curve 2 Sulfolane + propylenecarbonate, curve 3 Sulfolene + dimethyl sulfoxide

For the melting point determination, were the cryoscopy curves (instantaneous temperature dependence on time) used. The sample, closed in the glass battle, was inserted in ethanol bath. Into the sample was putted a thermocouple K type for temperature range from -250°C to 350°C. How is it shown on figure 2. The ethanol bath was cooled by liquid nitrogen on temperature approximately 10 °C lower than the supposed melting point. From the cryoscopy curves plateaus was the melting point, for each sample, determined. The numerical values of melting point are shown in table II.

Table II. – Melting point of solvents mixtures

Sulfolane concentration [%]	T_t [°C] sulfolane + ethylene carbonate	T_t [°C] sulfolane + dimethyl sulfoxide
0	35.9	16.9
20	20.6	7.8
40	-4.0	-5.3
60	-17.9	-20.8
80	-26.1	-12.7

The values of temperature shown in table II are the avarage results obtained from five measurment on the same sample. The samples were just mixtures of two solvents without a salt.

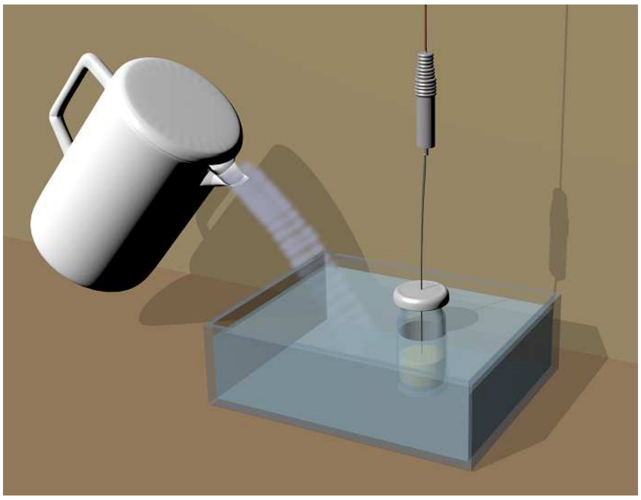

Fig. 2. Workplace organization for melting point measurment

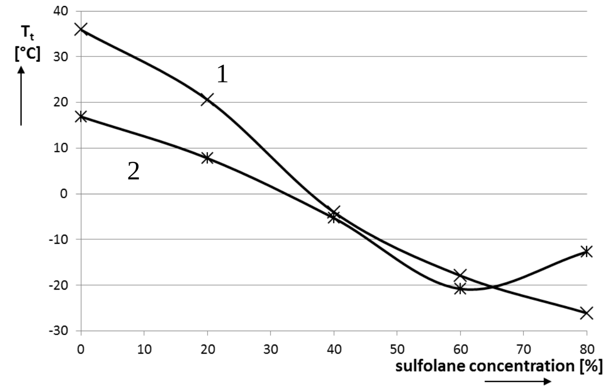

Fig. 3. The melting point dependance on concentration of sulfolane, curve 1 with ethylene carbonate, curve 2 witn dimethyl sulfoxide

On curve 2 (Fig. 3) is visible eutectic minimum of sulfolane dimethyl sulfoxide mixture and that by 60 vol.% of sulfolane. This minimum is slightly below -20°C. No such minimum was visible on sulfolane ethylene carbonate mixture.

The specific conductivity was determined by impedance spectroscopy measurement at indoor conditions. The values was determined from equivalent circuit parts fitted for obtained Nequist graph. The equivalent circuit was R1+Q1. From result Nequist graph was selected the most linear part at low frequencies and applied the fitting on chosen equivalent circuit. The calculation of impedance and all part was by help of equation 3

$$Z(f) = R_1 + \frac{1}{Q_1 (j2\pi f)^{\alpha_1}} \qquad (3)$$

where R_1 is the electrolytes resistivity, *Q1* is the konstant phase source, f is the frequency. The impedance spectroscopy was made in frequency range from 1 MHz to 100 Hz. Two platinum electrode conductivity cell covered by platinum black was used for measurement. All samples have the same concentration of dissolved salt 1 $\text{mol}\cdot\text{l}^{-1}$ of $LiClO_4$. At first was the saturation of dimethyl sulfone in the second solvent assessed. At first the samples, with volume concentration of dimethyl sulfone from 5% to 30% in five per cent step were prepared. The samples were heated on temperature slightly above the melting temperature of dimethyl sulfone and after ideal mixing they have been let too cold at room condition. After the cooling was visual detected in with samples, the dimethyl sulfone, were again recrystallized. The interval between two samples in with the dimethyl sulfone has and hasn't recrystallized was spitted more precisely in our case in 1% steps. The sample testing was re-enactment and the saturation border of dimethyl sulfone in second solvent was determined. The results values are in table III.

Table III. – Dimethyl sulfone saturation limit

Dimethyl sulfone	
Second solvent	Volume saturation concentration [%]
Sulfolane	17
propylene carbonate	15
ethylene carbonate	25
dimethyl carbonate	5
dimethyl sulfoxide	26

The highest specific conductivity reach the dimethyl sulfone (DMSO) and ethylene carbonate mixture, with was almost ten times higher than the rest of samples. The results are shown in figure 4.

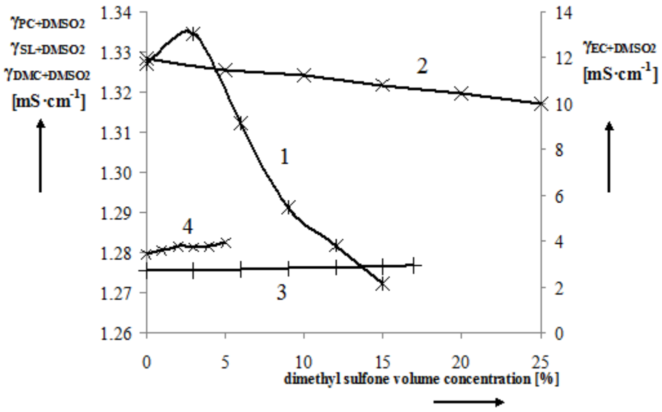

Fig. 4. The specific conductivity dependence on dimethyl sulfone concentration, 1 with prpylen carbonate, 2 with ethylen carbonate, 3 with sulfolane, 4 with dimethyl carbonate

The relative permittivity was measured by help of plate capacitor. The capacity of air was measured C_0 and then the capacity of the same capacitor filled by the electrolytes as the dielectric material C_d the permittivity of the electrolytes was calculated form this capacity by equation 4.

$$\varepsilon_r = \frac{C_d}{C_0} \qquad (4)$$

Samples with different volume ratio of sulfolane and dimethyl sulfone ware measured. Again all samples have the same salt concentration of lithium perchlorate 1 $mol\cdot l^{-1}$. The measured values are shown in table IV. The permittivity value was taken by measuring frequency 1 MHz.

Table IV. – Relative permittivity of electrolytes

Sample	ε_r [-]
0 vol.% DMSO	87.5
12 vol.% DMSO	83.9
15 vol.% DMSO	80.3

3. Conclusion

From solvents mixtures with are measured is clary that adding sulfolene into mixture increase the flash point. This material change and electronic protection with are used in modern lithium – iont batteries improve the fire safety of batteries. By using a solvents with higher flash point also can increase the work temperature of the battery and that allow us to use higher charge and discharge currents and that reduce the time needed to battery charging. Disadvantage of sulfolane is its high melting point (27.5°C) and that decrease the temperature use window in which the battery can work reliably. The melting point can be reduced due sulfolane high cryoscopy constant 85.6 $K\cdot kg\cdot mol^{-1}$ by adding salt with is important for electrolyte function, even by blend a second solvent into sulfolane rapidly sink the melting point under zero temperature what can be seen in figure 3. From table III is clary that with higher permittivity of the second solvent added in to dimethyl sulfone increases the saturation level of dimethyl sulfone. The best results show the mixture of ethylene carbonate and dimethyl sulfone. The combination of sulfolane and dimethyl sulfone is suitable for the batteries with work always at elevated temperature e.g. in the near of heating devices.

Appropriate combination of solvents it is possible to reach sufficiently high specific conductivity for use in batteries. The permittivity of measured electrolytes fulfils the condition $\varepsilon_r > 30$ and that almost three times.

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