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Causes of the double maximum conductivity of nanocomposite polymer electrolytes for lithium power sources

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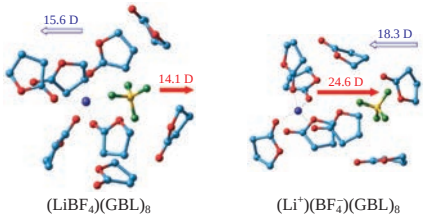
Causes of the double maximum conductivity of nanocomposite net electrolytes in the presence of SiO_2 nanoparticles (7 nm) were revealed by differential scanning calorimetry and quantum-chemical modeling. The first maximum results from increasing the dissociation of lithium salt, whereas the second one is due to the formation of conductive paths involving SiO_2 nanoparticles.



Nanocomposite polymer electrolytes usually exhibit a maximum on the ionic conductivity as a function of the amount of nanopowder introduced, which is caused by the formation of conductive paths involving nanoparticles.[1] In some systems, a second maximum appears at a lower concentration of nanoparticles, and it probably results from the enhancement of the ionic dissociation of a lithium salt in the presence of inorganic oxides. Thus, two maxima were observed in thickened gel electrolytes based on polymethylmethacrylate and polyethylene oxide with the addition of SiO_2 nanopowder (Aerosil 380) with an average particle size[2–6] of 7 nm or with the addition of larger (< 100 nm) Al_2O_3 or MgO_2 particles.[7–8] There is no direct evidence that the first maximum is due to ionic dissociation; therefore, it is of interest to investigate the dependence of the phase state of a nanocomposite electrolyte on the concentration of nanoparticles by differential scanning calorimetry (DSC). Previously, it was shown[9–10] that DSC is a very informative method for studying liquid aprotic electrolytes, although there is unclear which process corresponds to a particular peak. Therefore, it is desirable to use quantum-chemical modeling.

Here we carried out a complex study of the transparent films of nanocomposite polymer electrolytes (NPEs)† based on diacrylate polyethylene glycol (PEG-DA, M_n = 575), 1 M $LiBF_4$ solution in γ-butyrolactone (GBL) with the addition of SiO_2 (up to 12 wt%; hydrophilic Aerosil 380; pH 3.6–4.3 in a 4% aqueous dispersion; average particle size, 7 nm). In this system, $LiBF_4$:GBL molar ratio is ~1:12.

† The NPE films were synthesized using a radical polymerization reaction initiated by benzoyl peroxide. The $LiBF_4$ salt was dissolved in GBL, and then 15 wt% PEG-DA and 1 wt% benzoyl peroxide were added. After benzoyl peroxide was completely dissolved, SiO_2 (1 to 12 wt%) was added and the mixture was stirred for 1 h. The resulting homogeneous mixture was poured into a reactor consisting of two parallel panes treated with an antiadhesive and cured at 60 °C for 3 h, 70 °C for 1 h, 80 °C for 1 h, and 120 °C for 1 h. This curing mode ensured the complete polymerization of PEG-DA.

The ion conductivity of thin-film polymer electrolyte samples was studied by electrochemical impedance spectroscopy in symmetric cells with stainless steel electrodes using a Z-2000 impedance meter (Elins, Russia). The specific conductivity was calculated using a published procedure.[11]

Figure 1 shows that the conductivity of the NPE films has a complicated dependence on the SiO_2 nanoparticle content: there are two maxima at 2 and 6 wt% SiO_2 about 4 mS cm^{-1} at 20 °C. The similar appearance of two maxima was previously noted only in thickened gel electrolytes,[2–6] whereas this effect in the net electrolytes obtained by radical polymerization was revealed for first time.

To understand reasons for the appearance of two maxima, DSC and quantum-chemical modeling were used. DSC diagrams were recorded on a DSC 822e Mettler-Toledo device with initial sample cooling to –150 °C with liquid nitrogen; then, the sample was heated at a rate of 5 K min^{-1}. Figure 2 shows the DSC diagrams of NPE compositions with the addition of 12 wt% SiO_2, liquid electrolyte, and 1 M $LiBF_4$ in GBL.

The glass transition temperatures (T_g) measured for all of the NPEs were equal to that of the liquid electrolyte (–133 °C). The polymer matrix forms a slightly crosslinked network at 15 wt% PEG-DA; for this reason, there is no polymer glass transition process. Both liquid and polymer electrolytes without SiO_2 have two exothermic and one endothermic peaks close in shape. The latter at –50 °C refers to the melting of GBL, and two exothermic peaks are caused by the crystallization of the solvent in an amorphous phase produced under fast freezing.[9,10,12,13]

The ratio between the areas of the first and second exothermic peaks in the DSC curves of the liquid and polymer electrolyte without SiO_2 was 95:5. With the addition of 1, 2, 3 or 4 wt% SiO_2, this ratio becomes 65:35, 62:38, 80:20 or 76:24, respec-

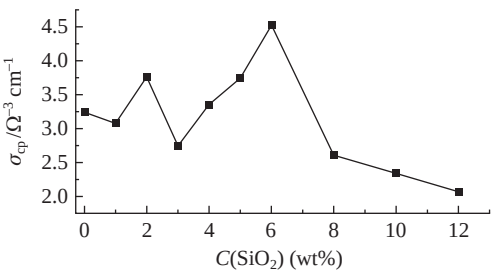


Figure 1 Conductivity of NPE *vs.* the SiO_2 content.

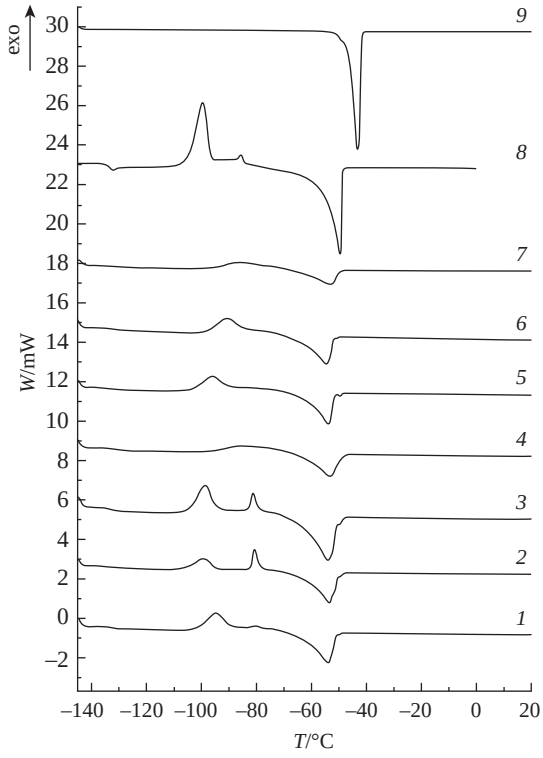


Figure 2 DSC diagrams of NPEs (*1*) without SiO_2 and with the introduction of (*2*) 2 wt%, (*3*) 4 wt%, (*4*) 6 wt%, (*5*) 8 wt %, (*6*) 10 wt%, (*7*) 12 wt% SiO_2, (*8*) 1 M $LiBF_4$ in GBL and (*9*) pure GBL for comparison.

tively. Thus, the relative area of the second exothermic peak is maximal at 2 wt% SiO_2, when the first maximum conductivity is achieved (see Figure 1).

Under the fast freezing of gel electrolyte, the solvent molecules do not have time to occupy the equilibrium positions intrinsic to a solid phase of GBL. Therefore, on a slow heating of the system, their relaxation is accompanied by the release of heat of a phase transition from an amorphous to a crystalline solid. It can be assumed from general considerations that in a sufficiently concentrated solution of 1 M $LiBF_4$ in GBL the predominant salt fraction exists as the ion pairs $Li^+BF_4^-$. Therefore, the exothermic peak of a larger area can be attributed to the crystallization of solvent associated with ion pairs, and the second peak of a smaller area, to the crystallization of solvent associated with free ions. This interpretation is consistent with a change in the conductivity of the nanocomposite electrolyte.

The general reason for the effect of nanoparticles on the ionic dissociation of salt is apparently related to the orienting action of highly polar bonds on the inorganic oxide surface. As a result, the thermodynamic characteristics of electrolytic dissociation are changed. At the same time, an increase in the number of nanoparticles leads to a decrease in the distance between them to obstruct the mobility of charged particles, and the total conductivity begins to fall. Note that the appearance of the second conductivity maximum is typical of SiO_2 nanoparticles with a porous structure, whereas the particles possessing a smooth surface, for example, SiO_2 (12 nm), exhibited only one conductivity maximum.[14]

To reveal the relationship between the degree of ionic dissociation and the first maximum of conductivity, the quantum-chemical modeling was performed using the density functional theory. The nonempirical exchange-correlation functional Perdew–Burke–Ernzerhof (PBE)[15] and the extended basis sets H [6*s* 2*p* / 2*s* 1*p*], C, O, B, F [10*s* 7*p* 3*d* / 3*s* 2*p* 1*d*], Li [10*s* 7*p* 3*d* / 4*s* 3*p* 1*d*] were used. This approach was tested in a study of the structure of Li^+ solvate

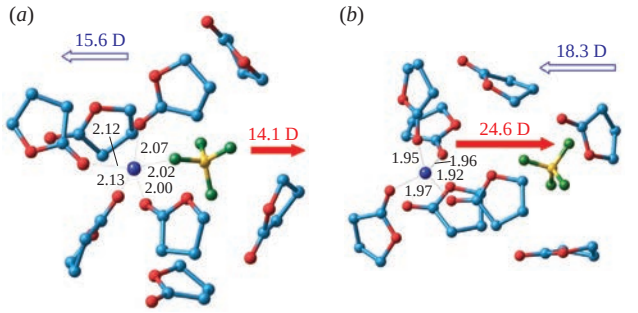


Figure 3 Structures of the solvate complexes (*a*) $(LiBF_4)(GBL)_8$ and (*b*) $(Li^+)(BF_4^-)(GBL)_8$. The empty and filled arrows indicate the dipole moments of $(GBL)_8$ and $LiBF_4$ subsystems, respectively.

complexes with crown ethers.[16] The calculations were performed using the PRIRODA program package[17] and computational facilities of the Joint Supercomputer Center of the Russian Academy of Sciences.

The energies and structures of the solvate complexes of ions (Li^+, BF_4^-) and the contact ion pair ($Li^+BF_4^-$) with eight GBL molecules were calculated. The dipole moments of these systems (5.4 and 3.4 D, respectively) are of the same order of magnitude as that of the cluster $(GBL)_8$ (4.1 D). The fact that the dipole moment of the separated ions is obviously higher than that of the contact ion pair indicates the much higher ordering of solvent molecules in the solvated shells of separated ions.

To quantitatively characterize this effect, we calculated the dipole moments of the $Li^+BF_4^-$ and $(GBL)_8$ subsystems with a fixed geometry corresponding to the solvate complexes $(LiBF_4)(GBL)_8$ and $(Li^+)(BF_4^-)(GBL)_8$ (Figure 3). From the values of the dipole moment of $(GBL)_8$ cluster, 15.6 and 18.3 D, respectively, larger ordering of the solvent molecules around the separated ions is seen. In this case, the dipole moments of the GBL molecules countervail the dipole moments of the ions Li^+ and BF_4^- (24.6 D), but not completely. Thus, the electric field of a large dipole $Li^+BF_4^-$ will be stronger counteract the reorientation of solvent molecules of the solvate shell, which is necessary for the formation of a crystalline phase with a zero dipole moment of the unit cell.[18] This leads to an increase in the temperature at which a second exothermic peak is observed.

Thus, based on quantum chemical calculations, we attributed the first wide exothermic peaks (–95 to –99 °C) to the crystallization of free solvent or weakly coupled solvate shells around $Li^+BF_4^-$ ion pairs and the second narrow exothermic peaks (–80 to –89 °C), to strongly bound solvent molecules in the solvate shells of Li^+ and BF_4^- ions.

Upon addition of 6 wt% SiO_2 and higher, the character of the DSC curves varies significantly (see Figure 2), and both exothermic peaks merge into one very broad peak with a maximum at –85 to –96°C. The appearance of the second maximum at 6 wt% SiO_2 is associated with the formation of extended conducting channels near the surfaces of SiO_2 particles. An increase in the concentration of nanoparticles and, accordingly, in the solvent volume in their surface layer led to the inhomogeneity of a phase transitions corresponding to the first and second exothermic peaks to cause their merging.

Thus, we conclude that the appearance of two maxima in the dependence of NPE conductivity on the concentration of nanoparticles is caused by a nonmonotonic change in the dissociation degree of the lithium salt. This effect seems to be a common feature of NPEs exhibiting two conductivity maxima.

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