SAXS/DSC/WAXD Study of Temperature Evolution in Nanocomposite Polymer Electrolytes with Different Nanofillers

A. Turković[1], P. Dubček[1], K. Juraić[1] and S. Bernstorff[2*]

[1]*Institute "Ruđer Bošković", P.O.Box 180, HR-10002 Zagreb, Croatia*
[2]*Sincrotrone Trieste, Strada Statale 14, km 163.5 Basovizza, 34149 Trieste, Italy*
Corresponding author: bernstorff@elettra.trieste.it , Tel. 00390403758572, fax 00390409380902
other authors: turkovic@irb.hr, dubcek@irb.hr

Abstract

Polymer electrolytes are nanostructured materials which are very attractive components for batteries and opto-electronic devices. $(PEO)_8ZnCl_2$ polymer electrolytes were prepared from PEO and $ZnCl_2$. The nanocomposites $(PEO)_8ZnCl_2$ themselves contained TiO_2, Al_2O_3, MgO, ZnO and V_2O_5 nanograins. In this work, the influence of the Al_2O_3, MgO and V_2O_5 nanograins on the morphology and ionic conductivity of the nanocomposite was systematically studied by transmission small-angle X-ray scattering simultaneously recorded with wide-angle X-ray diffraction and differential scanning calorimetry at the synchrotron ELETTRA (Trieste, Italy). These three measurement methods yielded insight into the temperature-dependent changes of the grains of the electrolyte. The heating and cooling rate was 0.5 °C/min. Environment friendly galvanic cells as well as solar cells of the second generation are to be constructed with such nanocomposite polymer as electrolyte.

.

Keywords: Polymer electrolytes, nanofillers, SAXS, WAXS, DSC

Introduction

Electromagnetic radiation can be used to obtain information about materials whose dimensions are of the same order of magnitude as the radiation wavelength. Since the larger the diffraction angle the smaller the length scale probed, wide angle X-ray diffraction (WAXD) is used to determine the crystal structure on the atomic length scale while small-angle X-ray scattering (SAXS) is used to explore the microstructure on the nanometer scale.

SAXS experiments are suitable to determine the structure of nanocomposite polymer electrolyte. Polymeric complexes of $(PEO)_n$ with $ZnCl_2$ have been used, due to their stability and very high conductivity [1,2]. Our research is aimed at optimizations of the electrolyte properties [3-8] as these materials are attractive as electrolytes for second generation of polymer-based rechargeable batteries [9, 10].

The aim of the present investigation was to study the temperature behavior of the nanocomposite $(PEO)_8ZnCl_2$ electrolyte by simultaneous SAXS, WAXD and differential scanning calometry (DSC). This structural investigation will provide an answer to the question about the behavior of this nanosized material through the superionic phase transition, which occurs at ~65 °C.

Experimental

The polymer-salt complex was prepared by dissolving $ZnCl_2$ (p.a. Merck) and poly(ethylene oxide) (laboratory reagent, BDH Chemicals, Ltd., Poole, England, Polyox WSR-301, MW=4x106, Prod 29740) in 50 % ethanol-water solution in stoichiometric proportions [3].

Simultaneous SAXS/WAXD/DSC measurements were performed at the Austrian SAXS beamline at the synchrotron ELETTRA, Trieste [11]. A photon energy of 8 keV was used, and the size of the incident photon beam on the sample was 0.1 x 5 mm^2 (h x w). For each

sample, SAXS and WAXD patterns were measured simultaneously in transmission setup using two 1D single photon counting gas detectors.

An in-line micro-calorimeter built by the group of Michel Ollivon (CNRS, Paris, France) [12] was used to measure simultaneously to SAXS/WAXD also high sensitivity DSC from the same sample position. The DSC phase transition temperature was determined at the intersection of the tangent to the peak and the baseline.

SAXS is observed when electron density inhomogeneities of nanosized objects exist in the sample. If identical grains of constant electron density ρ are imbedded in a medium of constant ρ_0, only the difference $\Delta\rho=(\rho-\rho_0)$ will be relevant for scattering. The amplitude is proportional to $\Delta\rho$ as only the contrast to the surrounding medium is effective. For the central part of the scattering curve, the universal Guinier approximation for all types of scattering objects/grains is valid [13-17]:

$$I_1(s) = \frac{1}{2\pi}(\Delta\rho)^2 \exp^{\left(-4\pi^2 s^2 R^2/3\right)} \qquad [1]$$

where R is the gyration radius which is the average square distance from the centre of masses within the particles.

Results

Figure 1 shows SAXS pattern which were obtained from polymer electrolyte $(PEO)_8ZnCl_2$ nanocomposite with three different nanofillers. The evolution of the average radii of the grains obtained by applying equation [1] is compared to the corresponding DSC and WAXD spectra behaviour (Figures 2 and 3).

In the heating cycle the superionic phase transition can be seen as the sudden drop of the nanograin sizes at the phase transition temperature. In the cooling cycle a hysteresis can be seen as the phase transition occurs at lower temperature. The endothermic and exothermic

peaks found in DSC during the same temperature cycle follow the sudden changes in the average nanograin sizes as obtained from the SAXS measurements and drops of the intensity in the WAXD spectra. In the heating cycle with rate of 0.5 °C/min in the SAXS data there are two trends, first an increasing of the grain size up to 74°C and then a sudden drop at this phase transition temperature.

The DSC spectrum shows that the phase transition temperature is 66.8°C for $PEO)_8ZnCl_2$ $/Al_2O_3$, which is determined at the beginning of the peak in the heating cycle. This temperature is the melting temperature of the PEO crystallites i.e. "spherulites" [18]. In the case of the nanocomposite polymer electrolyte, combined forms of PEO, $ZnCl_2$ and the three different nanofillers (Al_2O_3, MgO and V_2O_5) influence the melting temperature. Both, the SAXS and DSC data show a hysteresis, i.e. much lower phase transition temperatures (i.e. crystallization temperatures) than 65°C in the cooling cycle.

The WAXD recordings were done simultaneously with the SAXS and DSC measurements. Above the phase transition temperature the WAXD spectra are registering the amorphous phase of the polymer electrolyte. The WAXD data are giving the information of the side chain order. During the heating and cooling cycles the side chain ordering is giving us information of the lateral domain sizes or "spherulites". The WAXD results for all heating and cooling rates are, together with SAXS and DSC data, presented in the Table 1.

The combination of the three measuring methods reveals the nature of the physical transformation of the polymer electrolyte into a super ionic conductor. The nanocomposite crystalline and amorphous polymer matrix is turning into an amorphous highly conductive phase. In contrast to WAXD, which exhibits lines and crystalline grains only for the low temperatures crystalline phases, SAXS is showing the existence of nanograins in both the

low and high temperature phase. At the phase transition temperature the grain size changes, it is becoming smaller at higher temperatures. The nature of the nanograins as seen by SAXS is not just the pure crystalline, but also the partly amorphous form, while WAXD records only pure crystalline nanograins. Thus the picture of the highly conductive phase consists of a completely amorphous polymer matrix, which is known to be suitable for ion–conduction by elastic movement of PEO chains, and of nanograins of combined PEO/$ZnCl_2$ and $ZnCl_2$ structures, which could also contribute to Zn^{2+}-ion conduction by a hopping mechanism. Under proper circumstances, the presence of ion-transport pathways can be as important as polymer segmental motion [19,20].

Conclusion

The combined SAXS/WAXD/DSC measurements have shown that the nanostructure of the nanopolymer electrolyte $(PEO)_8ZnCl_2$ is changing during the crystalline-amorphous phase transition to a highly conductive superionic phase. In samples with nanofillers, the conductivity is higher and the phase transition temperature lower than for pure $(PEO)_8ZnCl_2$, which are desirable properties for application in batteries. The significant role that the nanodimensions of the electrolyte material play in the Zn^{2+}-ion mobility was discussed. The combined SAXS/WAXD information about the evolution of the average grain sizes during the phase transition gave insight into the nanomorphology, which influences the ionic transport in a nanocomposite polymer electrolyte. Further optimizations of the electrolyte properties are in progress since these nanostructured materials are very attractive for batteries or other types of electronic devices

Acknowledgments

The Ministry of Education, Science and Sport of the Republic of Croatia is thanked for the support of this work.

References

1. T.M.A. Abrantes, LJ.Alcacer and C.A.C. Sequeira, *Solid State Ionics* **18/19** (1986) 315.
2. M.J.C. Plancha, C.M. Rangel and C.A.C. Sequeira, *Solid State Ionics* **116** 1999) 293.
3. A. Turković, M. Pavlović, P. Dubček, M. Lučić-Lavčević, B. Etlinger and S. Bernstorff, *J. Electrochem. Soc.***154/6** (2007) A554.
4. A. Turković, M. Pavlović, P. Dubček and S. Bernstorff, *Acta Chimica Slovenica* **55/4** (2008) 822.
5. A. Turković, M. Rakić, P. Dubček, M. Lučić-Lavčević and S. Bernstorff, *Vacuum* **84/1 (**2008) 68.
6. A. Turković, P. Dubček, K. Juraić, A. Drašner and S. Bernstorff, Materials, **3/11** (2010) 4979.
7. A. Turković, P. Dubček, K. Juraić, M. Rakić and S. Bernstorff, Journal of The Organic and Inorganic Polymers, 21, 1-5 (2011) DOI: 10.1007/s10904-011-9469-7, Online First.
8. A. Turković, P. Dubček, M. Rakić, M. Lončarić, B. Etlinger and S. Bernstorff, Vacuum, in press 2011.
9. S.J. Visco, M. Liu, L.C. Dejonge, Cell for making secondary batteries, *Patent number* 5162175, Nov.10, (1992);
10. F. Brochu, M. Duval, Additives for extruding polymer electrolytes, *Patent number*: 5622792 Apr 22, (1997).
11. H. Amenitsch, S. Bernstorff, P. Laggner, *Rev.Sci.Instr*. **66** (1995) 1624.
12. M. Ollivon, G. Keller, C. Bourgaux, D. Kalnin and P. Lesieur; *Journal of Thermal Analysis and Calorimetry* **85/1** (2006) 219.
13. *Small Angle X-ray Scattering*, O.Glatter, O. Kratky, Editors, Academic press, p 18. (1982).

14. A. Guinier, Ann.Phys. (Paris),**12**, (1939) 161.

15. G. Porod, Kolloid-Zeitschrift,**124**, (1951) 83.

16. G. Porod, Kolloid-Zeitschrift, **125**, (1952a) 51.

17. G. Porod, Kolloid-Zeitschrift, **125**, (1952b) 109.

18. I.Pucić and A.Turković, *Solid State Ionics* **176 (**2005) 1797.

19. P.G. Bruce, *Dalton. Trans.* **11** (2006) 1365.

20. E. Staunton, A.M. Cristie, I. Martin-Luis, Y.G. Andreev, A.M.Z. Slawin and P.G. Bruce, *Agnew. Chem., Int. Ed.* **43/16** (2004) 2103.

Figure Captions:

Figure 1. *SAXS results for nanocomposite polyelectrolyte $(PEO)_8ZnCl_2$ in the temperature range from 20°C to 100°C at rate of 0.5°C/min, for a) $PEO)_8ZnCl_2/Al_2O_3$; b) $PEO)_8ZnCl_2/MgO$ and c) $PEO)_8ZnCl_2/V_2O_5$.*

Figure 2. DSC results for nanocomposite polyelectrolyte $(PEO)_8ZnCl_2$ in the temperature range from 20°C to 100°C at rate of 0.5°C/min, for a) $PEO)_8ZnCl_2/Al_2O_3$; b) $PEO)_8ZnCl_2$ /MgO and c) $PEO)_8ZnCl_2/V_2O_5$.

Figure 3. *WAXD results for nanocomposite polyelectrolyte $(PEO)_8ZnCl_2$ in the temperature range from 20°C to 100°C at rate f 0.5°C/min, for a) $PEO)_8ZnCl_2/Al_2O_3$; b) $PEO)_8ZnCl_2/MgO$ and c) $PEO)_8ZnCl_2/V_2O_5$*

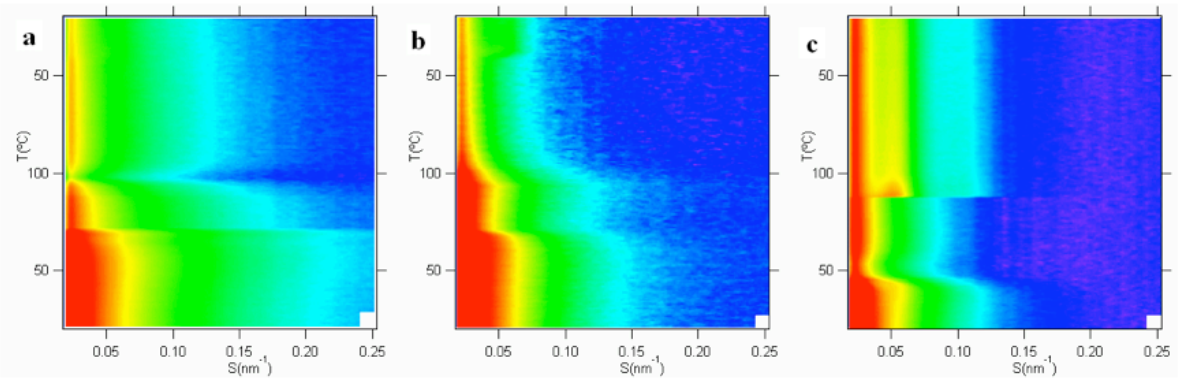

Figure 1

Authors: A. Turković, P. Dubček, K. Juraić and S. Bernstorff*

Paper Title: SAXS/DSC/WAXD Study of Temperature Evolution in Nanocomposite Polymer Electrolytes with Different Nanofillers

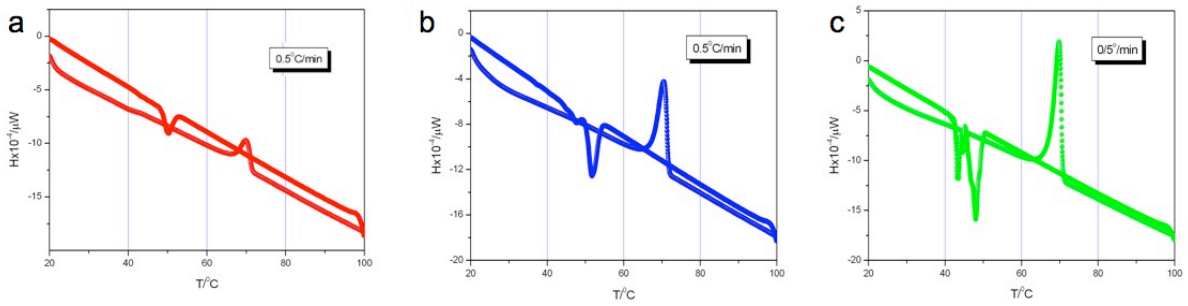

Figure 2

Authors: A. Turković, P. Dubček, K. Juraić and S. Bernstorff*

Paper Title: SAXS/DSC/WAXD Study of Temperature Evolution in Nanocomposite Polymer Electrolytes with Different Nanofillers

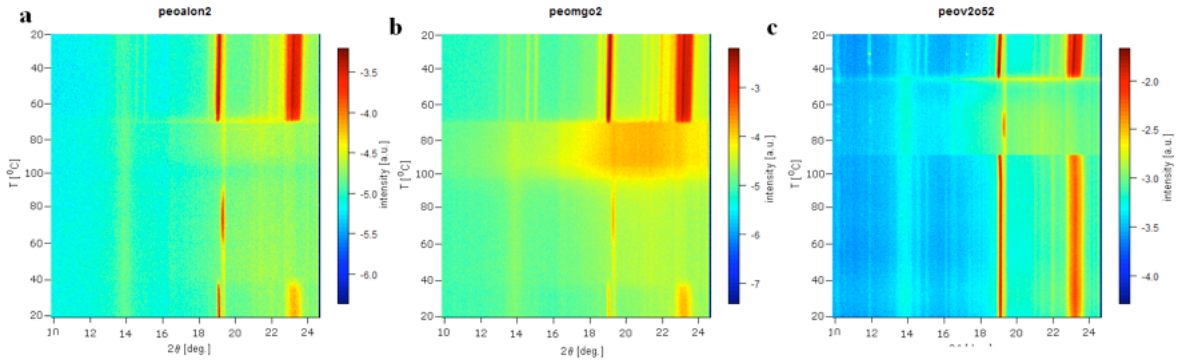

Figure 3

Authors: A. Turković, P. Dubček, K. Juraić and S. Bernstorff*

Paper Title: SAXS/DSC/WAXD Study of Temperature Evolution in Nanocomposite Polymer Electrolytes with Different Nanofillers

TABLE 1. Changes of average grain radius <R>/nm by SAXS and phase transition temperatures t (in °C) in $(PEO)_8ZnCl_2$ polyelectrolyte with different nanofillers (x) during heating and cooling as determined by SAXS/WAXS/DSC measurements.

$(PEO)_8ZnCl_2$ + x	heating			
	SAXS		WAXS	DSC
x/nm	t (°C)	<R> (nm)	t (°C)	t (°C)
Al_2O_3 /5.1	66.9	8.6-6.1	70.1	66.8
MgO /13.3	66.4	11.7-9.8	71.2	65.3
V_2O_5 /9.1	45.4	10.1-9.9	48.0	64.1
$(PEO)_8ZnCl_2$ +x	cooling			
	SAXS		WAXS	DSC
x /nm	t (°C)	<R> (nm)	t (°C)	t (°C)
Al_2O_3/5.1	42.5	5.7	39.6	52.5
MgO/13.3	39.3	6.3	39.8	54.4; 48.9
V_2O_5 /9.1	40.6	6.2	40.4	49.9; 45.3; 44.1