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Study of polymer electrolyte for Zn rechargeable nanostructured galvanic cells via combined in situ SAXS/DSC/WAXD measurements

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Abstract: Polymer electrolytes as nanostructured materials 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 to the morphology and ionic conductivity of the nanocomposite was systematically studied by transmission small-angle X-ray scattering (SAXS) simultaneously recorded with wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) at the synchrotron ELETTRA. The SAXS/DSC/WAXD measurements yielded insight into the temperature-dependent changes of the grains of the electrolyte. The heating and cooling rate was 1°C/min and ½°C/min (1). Environment friendly galvanic cells as well as solar cells of the second generation are to be constructed with nanocomposite polymer as electrolyte.

Keywords: Polymer Electrolytes, Nanocomposites, SAXS/DSC/WAXD

1. Introduction

Electromagnetic radiation can be used to obtain information about materials whose dimensions are on 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 ZnCl2 have been used, due to their stability and very high conductivity (2, 3). Our research was aimed at optimizations of electrolyte properties (4-9) as these materials are attractive as electrolytes for second generation of polymer-based rechargeable batteries (10, 11).

The aim of the present investigation was to study the temperature behavior of the nanocomposite electrolyte (PEO) 8ZnCl2 with different nanofillers Al2O3, MgO and V2O5 by simultaneous SAXS/WAXD/DSC measurements. This structural investigation will provide answer to the question about the behavior of nanosizes through the superionic phase transition, which occurs at ~65 °C.

2. Experimental

The polymer-salt complex was prepared by dissolving ZnCl2 (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 with addition of Al2O3, MgO and V2O5 nanograins (4). The polymer-salt complex solution was then poured onto a Teflon plate and resulting film dried, first in air, and then in vacuum of 10-6 mbar for 7 days and then stored in desiccators.

Simultaneous SAXS/WAXD/DSC measurements were performed at the Austrian SAXS beamline at the synchrotron ELETTRA, Trieste (12). Photon energy of 8 keV was used, and the size of the incident photon beam on the sample was 0.1 x 5 mm2 (h x w). For each sample, SAXS and WAXD patterns were measured simultaneously

in transmission setup using two 1D single photon counting gas detectors.

The in-line micro-calorimeter built by the group of Michel Ollivon (CNRS, Paris, France) (13) was used to measure simultaneously SAXS/WAXD and high sensitivity DSC from the same sample. DSC phase transition temperature was determined at the intersection of 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 ρ0, only the difference Δρ=(ρ-ρ0) will be relevant for scattering. The amplitude is proportional to Δρ 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 (14-16):

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

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

3. Results

Fig. 1 shows the SAXS measurements on polymer electrolyte (PEO)8ZnCl2 nanocomposite with three nanofillers (Al2O3, MgO and V2O5) which were performed simultaneously with rate of 1°C/min at the SAXS-beamline of ELETTRA. The evolution of the average radii of grain sizes obtained by applying SAXS equation [1] is compared to the corresponding DSC and WAXD spectra behavior.

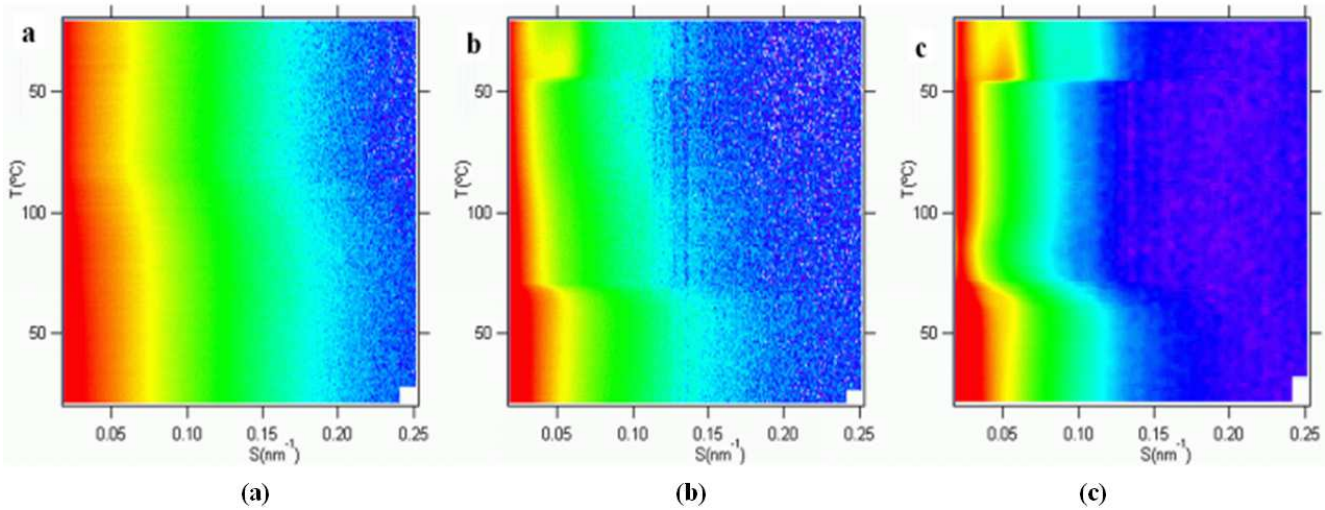

Figure 1. *SAXS results for nanocomposite polyelectrolyte $(PEO)_8ZnCl_2$ in the temperature range from 20°C to 100°C at rate of 1°C/min, for a) $(PEO)_8ZnCl_2/Al_2O_3$; b) $(PEO)_8ZnCl_2$/MgO and c) $(PEO)_8ZnCl_2/V_2O_5$.*

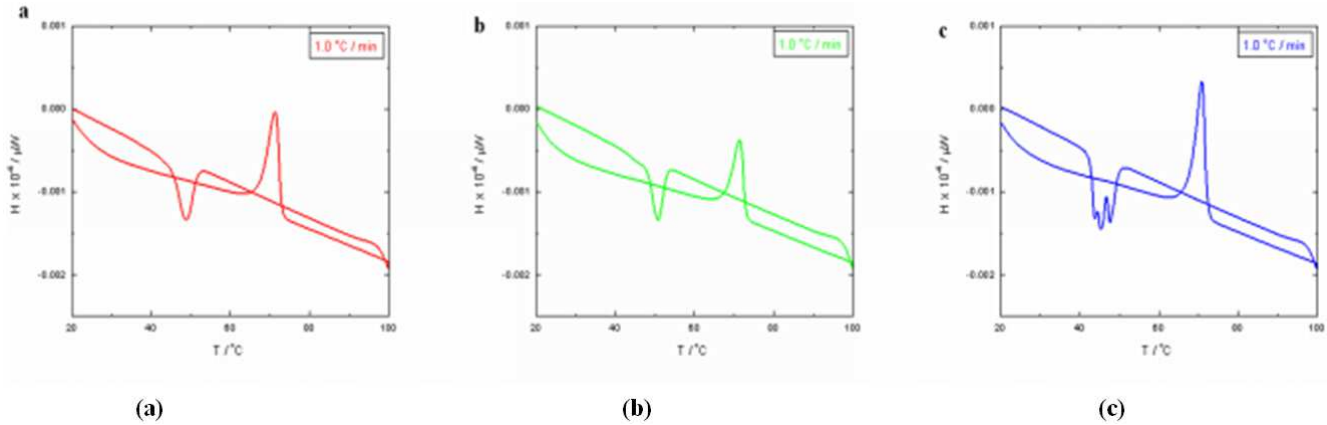

Figure 2. *DSC results for nanocomposite polyelectrolyte $(PEO)_8ZnCl_2$ in the temperature range from 20°C to 100°C at rate of 1°C/min, for a); $PEO)_8ZnCl_2/Al_2O_3$; b) $PEO)_8ZnCl_2$/MgO and c) $PEO)_8ZnCl_2/V_2O_5$*

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 part 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 1 °C/min in the SAXS data there are two trends, first an increasing of the grain size up to 64.1°C for PEO)8ZnCl2 /Al2O3 and then a sudden drop at this phase transition temperature.

The DSC spectrum for the rate of 1°C/min shows that the phase transition temperature is 66.9°C, which is determined at the beginning of the peak in the heating cycle. Both, the SAXS and DSC data show a hysteresis, i.e. much lower phase transition temperatures than 65°C in the cooling cycle. This temperature is the melting temperature of the PEO crystallites i.e. "spherulites" (17).

The WAXD recordings were done simultaneously with the SAXS and DSC measurements. Above the phase transition temperature of 65.3°C, 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".

SAXS measurements with rate of ½°C/min on polymer electrolyte (PEO) 8ZnCl2 nanocomposite for three nanofillers Al2O3, MgO and V2O5 were presented in previously published paper (1). These results are compared with results for the experiment with heating rate of 1°C/min in the Table 1.

Table 1. *Changes of average grain radius <R>(nm) by SAXS and phase transition temperatures T / °C in (PEO)8ZnCl2 polyelectrolyte with different nanofillers (x) during heating and cooling as determined by SAXS/WAXS/DSC measurements.*

(PEO)8ZnCl2/ x	heating /rate 1°C/min				heating /rate ½°C/min (1)			
	SAXS		WAXS	DSC	SAXS		WAXS	DSC
x(nm)	t (°C)	<R> (nm)	t (°C)	t (°C)	t (°C)	<R> (nm)	t (°C)	t (°C)
Al2O3 /5.1	64.1	5.1-4.7	65.3	66.9	66.9	8.6-6.1	70.1	66.8
MgO /13.3	62.2	11.0-10.2	66.4	67.2	66.4	11.7-9.8	71.2	65.3
V2O5 /9.1	42.5	10.5-8.3	63.5	66.8	45.4	10.1-9.9	48.0	64.1
(PEO)8ZnCl2/x	cooling /rate 1°C/min				cooling /rate ½°C/min (1)			
	SAXS		WAXS	DSC	SAXS		WAXS	DSC
x (nm)	t (°C)	<R> (nm)	t (°C)	t (°C)	t (°C)	<R> (nm)	t (°C)	t (°C)
Al2O3 /5.1	41.2	4.6	44.5	52.0	42.5	5.7	39.6	52.5
MgO /13.3	45.3	4.8	47.2	53.1	39.3	6.3	39.8	54.4; 48.9
V2O5 /9.1	40.7	5.2	45.5	50.2; 47.6	40.6	6.2	40.4	49.9; 45.3; 44.1

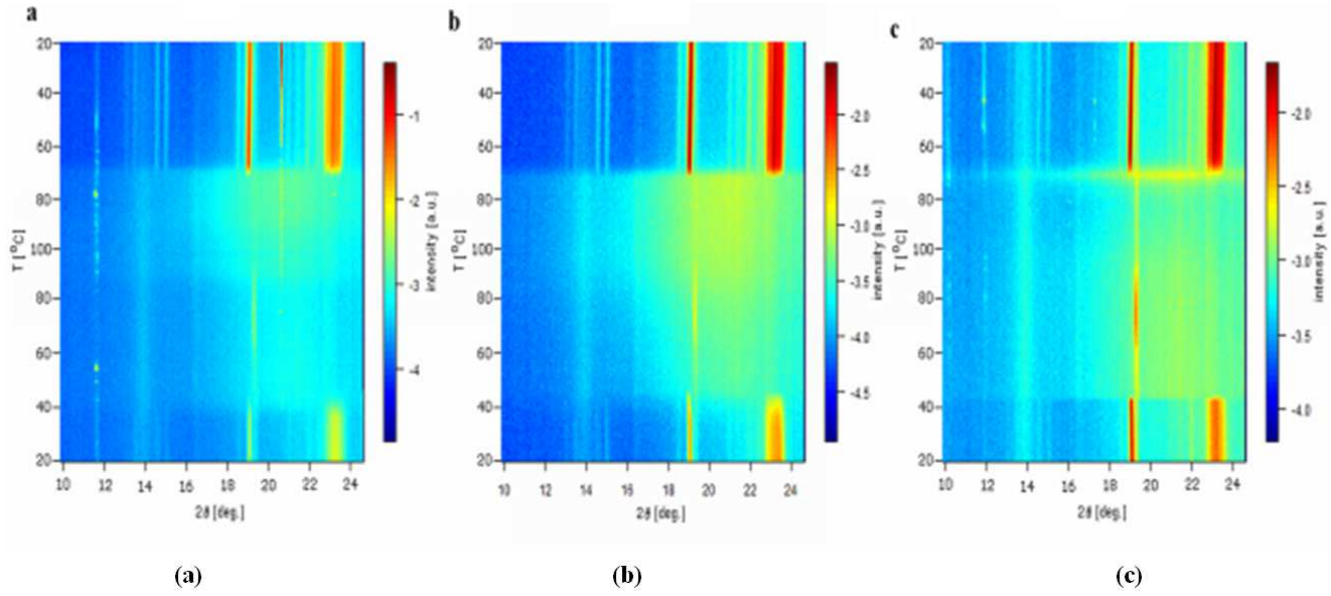

Figure 3. *WAXD results for nanocomposite polyelectrolyte $(PEO)_8ZnCl_2$ in the temperature range from 20°C to 100°C at rate of 1°C/min, for a) $PEO)_8ZnCl_2/Al_2O_3$; b) $PEO)_8ZnCl_2$/MgO and c) $PEO)_8ZnCl_2/V_2O_5$*

In the heating and cooling cycles, for both rates of ½°C/min and 1°C/min in the SAXS data, there are two trends, first an increasing of the grain sizes with temperature and then a sudden drop at the phase transition.

For both rates, the SAXS and DSC data show a hysteresis, i.e. much lower phase transition temperatures than 65°C in the cooling cycle. In the case of the nanocomposite polymer electrolyte, combined forms of PEO and ZnCl2, ZnCl2 and three different nanofillers (Al2O3, MgO and V2O5) influence the melting temperature. The WAXD recordings done simultaneously with SAXS measurements are showing the same trend of increasing phase transition temperature

upon heating and decreasing of it in cooling cycles for both heating rates. 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 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 in 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/ZnCl2 and ZnCl2 structures, which could also contribute to Zn2+-ion conduction by a hopping mechanism. Under proper circumstances, the presence of ion-transport pathways can be as important as polymer segmental motion (18, 19).

Comparing SAXS obtained phase transition temperatures in heating cycles for different fillers, we can observe that nanofiller V2O5 with average grain size of <R>=9.1 nm, is lowering this temperature to 42.5 °C and 45.4 °C for rates of 1°C/min and ½ °C/min, respectively. As our goal is to approach room temperature, which is the operating temperature for galvanic cells, this nanofiller is showing the best interaction with polymer matrix.

We are in the proces of constructing and characterizing galvanic cells using polymer electrolytes with here presented different fillers. The schematics of such cells are:

1. Zn/ (PEO) 8ZnCl2/[Al2O3])/ SnO2, TiO2

2. Zn/ (PEO) 8ZnCl2/[MgO])/ SnO2, TiO2

3. Zn/ (PEO) 8ZnCl2/[V2O5])/ SnO2, TiO2

The results of this future research will be presented in another paper.

4. Conclusion

The combined SAXS/WAXD/DSC measurements have shown that the nanostructure of the nanopolymer electrolytes (PEO)8ZnCl2 with different nanofillers (Al2O3, MgO and V2O5) are changing during the crystalline-amorphous phase transition to a highly conductive superionic phase. The conductivity is higher and the phase transition temperature lower than for the (PEO) 8ZnCl2, which are desirable properties for application in batteries. The significant role that the nanodimensions of the electrolyte material play in the Zn2+-ion mobility was discussed. The most promising results are obtained for nanopolymer electrolyte with V2O5 nanofiller. 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

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