Metal oxide nano-particles and nano-composite polymer electrolytes - electrodes and electrolytes in solar and galvanic cells of the second generation

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Nanocomposite polymer electrolytes and nanophased metal oxide films are tailored and used as electrodes and electrolytes in galvanic and solar cells of second generation. Nano-composites were prepared using PEO γ-irradiated to selected doses and TiO_2 nanograins, which treatments largely enhanced the conductivity of these polymer Zn^{2+}-ion conducting electrolytes. Metal oxide nanostructured films based on titanium, cerium and vanadium were investigated as possible working electrodes in solar or galvanic cells of second generation. As the most promissing and complete methods for investigation of morphology and structure of nanosize ordered materials, synchrotron small-angle X-ray scattering (SAXS) methods were applied to study both type of nano-materials.

Introduction

$(PEO)_8ZnCl_2$ polymer electrolytes and nano-composites were prepared using PEO γ-irradiated to selected doses and TiO_2 nanograins. The influence of added nanosize TiO_2 grains to polymer electrolytes and the effect of γ-radiation from a Co-60 source were studied by small-angle X-ray scattering (SAXS) simultaneously recorded with differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) at synchrotron ELETTRA. Infrared (IR) and impedance spectroscopy (IS) were also performed (1). We observed changes between 293 K and 373 K for treated and as prepared polymer electrolyte in SAXS/DSC/WAXD spectra and during the phase transition to the superionic phase at 335 K. Above-mentioned treatments largely enhanced the conductivity of polymer electrolyte. Room temperature conductivity increase up to two orders of magnitude was achieved.

Metal oxide nanostructured thin films were studied as electrodes for dye-sensitized solar cells and charge-discharge second generation batteries. We have studied materials based on titanium, cerium and vanadium (2). Materials based on titanium are nanocrystalline TiO_2 thin films, which play an important role in new generation of photochemical solar cells. Dye-sensitised cell differ from the semiconductor devices that they separate the function of light absorption from charge carrier transport. This cell was made of relatively non pure material with a cheap preparation procedure and energy conversion efficiencies ranging from 7 to 12%. Average grain sizes and specific surface areas as a function of temperature for TiO_2 samples annealed in oxydizing and non-oxydizing atmosphere were obtained by GISAXS measurements at synchrotron ELETTRA. Vanadium oxide, such as V_2O_5, has been extensively studied because it tends to form layered structure that allows the intercalation/de-intercalation of different ions between its layers. It can be used as catalysts, in electrochromic device, in an advanced electrochemical cell concept, especially in lithium batteries. We have also studied V/Ce films intercalated with Li^+-ions. 2D-GISAXS measurements revealed morphology change upon the intercalation of Li^+- ions. GIXR (grazing-incidence X-ray reflectivity) was used for determination of layer thickness.

The conductivity of $(PEO)_8ZnCl_2$ polyelectrolytes films can be significantly increased by radiation processing of poly(ethylene oxide) and addition of TiO_2 nano-grains. These treatments significantly increased conductivity of polyelectrolytes and lowered temperature of the phase transition.The results are stimulating for further research of PEO polyelectrolytes and nanocomposites and also gather information on underlying conductivity mechanisms. GISAXS at ELETTRA could be applied for determining grain size and porosity in TiO_2, CeO_2, V_2O_5 and V/Ce oxides on glass substrate as well as for following the process of intercalation of cations into the porous nanostructured films. The morphology obtained by modifying and choosing particular preparation is suitable for application in advanced electrochemical and efficient new solar cells. By means of electrical measurements, we have shown that polymer electrolyte $(PEO)_8ZnCl_2$ can be combined with V_2O_5-CeO_2 at 38 at.% of V as intercalation cathode in order to obtain all solidstate rechargeable galvanic cell. Further optimisations of electrolyte and electrodes properties are in progress.

Results and discussion

Nanocomposite polymer electrolytes

Original poly(ethilen-oxide), PEO was crosslinked with γ-irradiation ^{60}Co till selected doses and $(PEO)_8ZnCl_2$ polyelectrolyte films were prepared by dissolving of $ZnCl_2$ and PEO in stoichiometric proportions in 50% water–ethanol solution with and without addition of nanograins of TiO_2.

The crystallinity significantly decreased with addition of TiO_2 nanograins and radiation dose. Room temperature conductivity increase up to two orders of magnitude was achieved.

Characterizations of samples were preformed by: Electrical measurements: Impedance spectroscopy (IS), Impedance-analyzer - built in our laboratory, Optical methods: IR and Raman spectroscopy, Thermical measurements: Differential scanning calorimetry (DSC), Microscopy: Transmission electron microscopy, optical microscopy and SAXS/DSC/WAXD combined measurements at SAXS-beam line at synchrotron ELETTRA, Trieste.

Fgure 1. is showing TEM micrographs of crystalline spheric areas called “spherulites” in $(PEO)_8ZnCl_2$. Introducing 25 nm grains of TiO_2 these areas are broken to smaller pieces. The croslinking with γ-irradiation ^{60}Co is also breaking “spherulites”. The point of these treatments is to minimize crystalline parts of polymer as conductivity is enhanced throughout amorphous areas. The effect of these is shown on Figure 2 where conductivity of material treated with nanograins of TiO_2 and simultaneously crosslinked is highly conductive already above 40 °C, which temperature is close to ambient temperature at which galvanic cells operate. The combined three methods for investigating superionic phase transition in these materials are presented in Figure 3. This is nanocomposite showing a small nanograin sizes which indicate a large amount of amorphous phase in material. The phase transition occurs at 65 °C in SAXS data having hysteresis and in cooling cycle it is at 50°C. DSC shows it as 63 °C and 53 °C and WAXD 65 °C and 50 °C. The speed of heating and cooling in this example is 1°C/min.

Different rates of heating and cooling of 1°C/min, 3°C/min and 5 °C/min are presented and discussed in papers by Turković et al. (3,4).

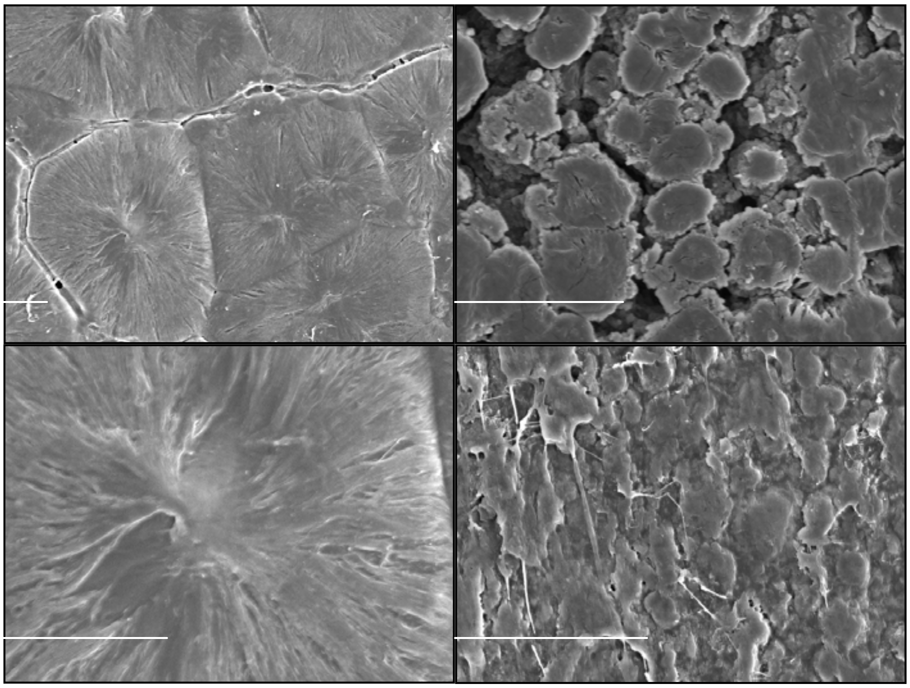

Figure 1. TEM microscopy of “Spherulites” in $(PEO)_8ZnCl_2$, $(PEO)_8ZnCl_2 + TiO_2$, one “Spherulite” and $(PEO)_8ZnCl_2$ crosslinked with γ-irradiation ^{60}Co. The scale is 100 µm.

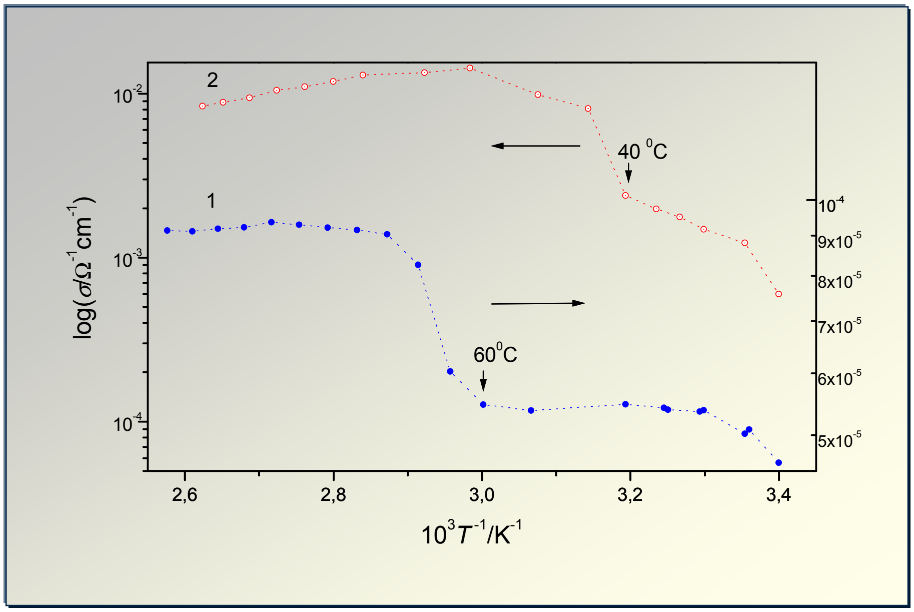

Figure 2. Impedance spectroscopy of (1) $(PEO)_8ZnCl_2$ and (2) $(PEO)_8ZnCl_2 + TiO_2$, crosslinked with γ-irradiation ^{60}Co.

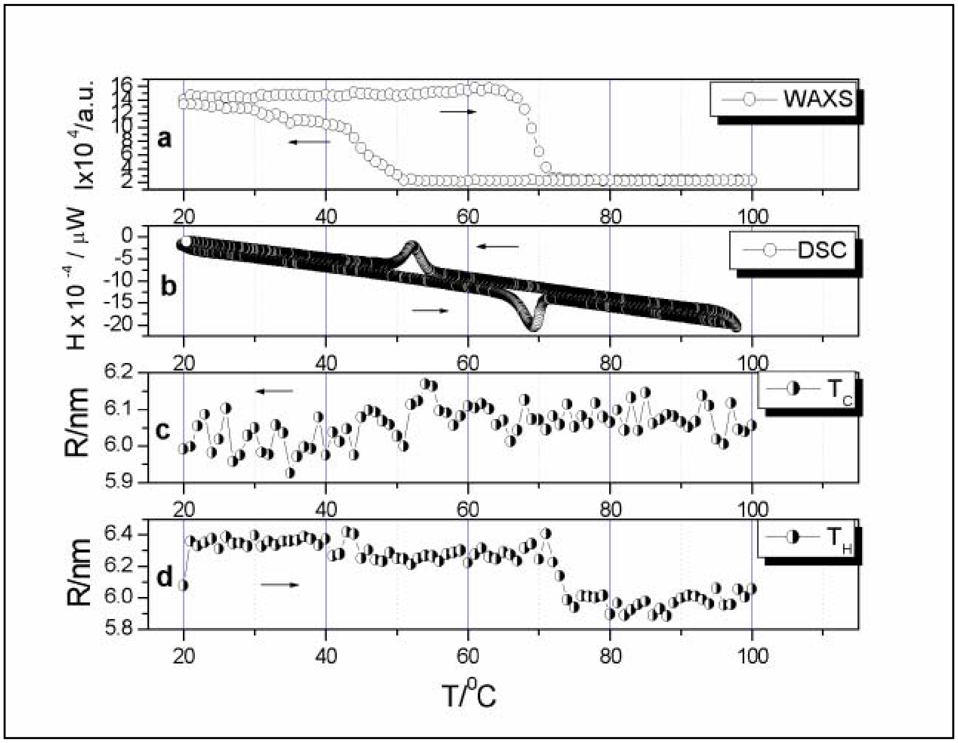

Figure 3. WAXD/DSC/SAXS of $(PEO)_8ZnCl_2$+TiO_2 rate 1°C/min.

Metal oxide nanostructured thin films

Materials based on titanium Nanocrystalline TiO_2 thin films play an important role in new generation of photochemical solar cells. Dye-sensitised cell differ from the semiconductor devices that they separate the function of light absorption from charge carrier transport. This cell was made of relatively non pure material with a cheap preparation procedure and energy conversion efficiencies ranging from 7 to 12%. Such solar cell mimics photosynthesis in leaf by chlorophyll. The last decade has been marked by the increasing interest for different preparations and characterizations of TiO_2 nanostructured films. A 10 μm thick, optically transparent film of titanium dioxide particles a few nanometers in size, coated with a monolayer of charge-transfer dye forms an electrode for the very efficient Grätzel´s solar cell.

The TiO_2 films prepared by sol-gel procedure were annealed in oxygen, nitrogen and hydrogen atmospheres in the temperature range between 373 K and after increasing to the anatase-rutile phase transition temperature of 1173 K (5).

Sample irradiated by X-rays scatters radiation. Each electron becomes the source of a secondary, scattered wave. The energy that electrons receive is much larger that bounding energy and they start to behave as free electrons. For the central part of the scattering curve, universal Guinier approximation for all types of the scattering objects (grains/particles) is valid:

$$I_1(q) = (\Delta n_e)^2 \exp\left(-\frac{q^2R^2}{3}\right) \qquad (1)$$

where R is gyration radii. It is the average square distance from the centre of mass, and role of mass is given to the electrons. The absolute value of the scattering vector equals $q=2\pi/\lambda \sin\theta$.

Grazing-incidence small angle X-ray scattering (GISAXS) spectra for each TiO_2 film are measured in reflection geometry (6-8) at nine different positions of sample regarding incident beam. The beam was gradually lowered to sample for nine positions ranging from 0.1 mm to 1 mm. Comparing to standard set-up in transmission geometry, in our experimental setting X-rays travel much longer through the film and therefore substrate signal I_s is depleted as $I_s \approx I_o exp-(\mu_F d_F)$ where Io is intensity of primary beam, μ_F is coefficient of absorption of film and d_F is film thickness. However, in this geometry, at lower positions of the beam, the scattering signal can be strongly affected by the substrate (9).

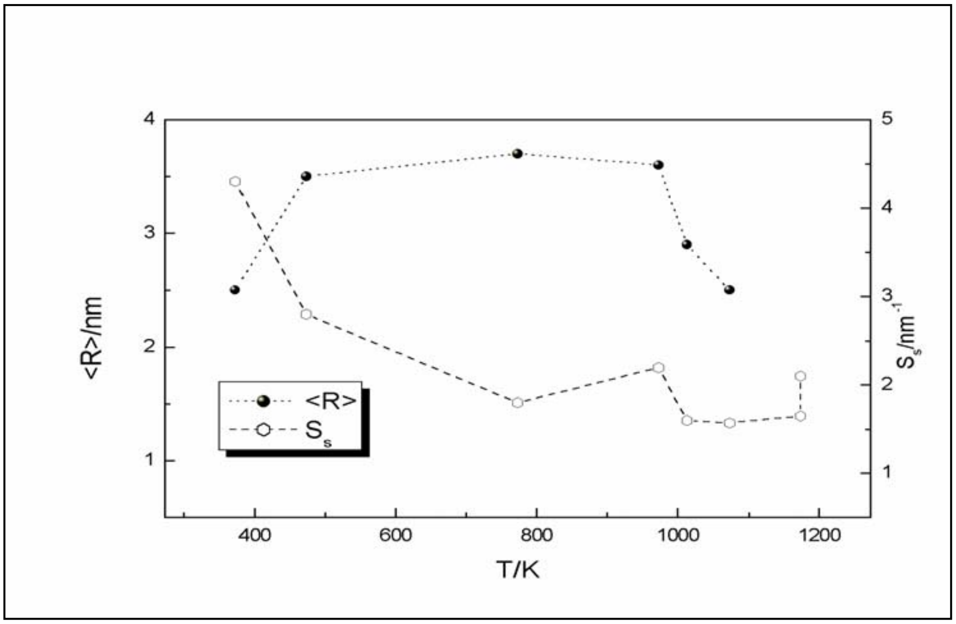

Figure 4. GISAXS: Average grain sizes and specific surface areas as a function of temperature for TiO_2 samples annealed in hydrogen atmosphere.

Materials based on cerium Nanosized CeO_2 and CeO_2-SnO_2 films were originally prepared for electrochromic display (10) and latter a Grätzel type solar cell was formed with that electrode (11). Among a number of available methods for depositing CeO_2 thin films, sol-gel dip-coating method was a promising prospect since it offers advantages in controlling the microstructure of films. The films were prepared with repeated dipping, which varied from 4 to 14 times. The film thickness depended on a number of dips and varied from 100 nm (for 4 dips) to 500 (for 14 dips) nm. It was determined by a Tencor-alpha-step instrument. Comparison of GISAXS obtained <R>, Ss and d values for CeO_2 films obtained with 8 dips and annealed at 773 K is shown on Figure 5. In XRD measurements (12) the crystallite or grain size of these films was estimated using the Scherrer equation

$$D=0.9\lambda/(\beta \cos \theta) \qquad (2)$$

where λ is the X-ray wavelength, θ is the Bragg angle and β is the pure full width of the diffraction line at half of the maximum intensity. Cerium based films were investigated as well as with 2D-GISAXS measurements at synchrotron ELETTRA (13-15).

Materials based on vanadium Vanadium oxide, such as V_2O_5, has been extensively studied because it tends to form layered structure that allows the intercalation/de-intercalation of different ions between its layers. It can be used as catalysts, in electrochromic device, in an advanced electrochemical cell concept, especially in lithium batteries. The addition of cerium improved stability of vanadium oxide with the ion-charge capacity (up to 30 $mCcm^{-2}$). The intercalation of Li^+ ions in V/Ce films was followed by FT-IR spectroscopy in combination with CV measurements at wide potential range. 2D-GISAXS measurements revealed morphology change upon the intercalation of Li^+ ions. Vanadium oxide, such as V_2O_5, has been extensively studied because it tends to form layered structure that allows the intercalation/de-intercalation of different ions between its layers.

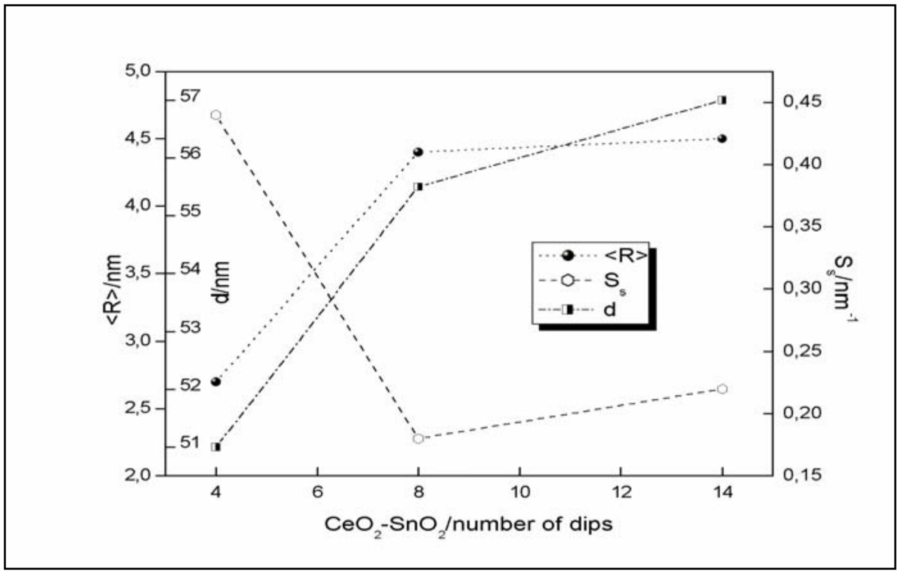

Figure 5. SAXS: Average grain sizes, specific surface and thickness of the films as a function of number of dips in sol-gel procedure of preparation for CeO_2 samples

It can be used as catalysts, in electrochromic device, in an advanced electrochemical cell concept, especially in lithium batteries (11). Our previous measurements of morphology of this material have shown its nanosized beside layered structure (5, 16). To make complete characterisation of interfaces in a layer structure of vanadium and V/Ce oxide films on glass substrates, we have performed grazing-incidence X-ray reflectivity (GIXR) [17]. We have compared GIXR characterization of layers with GISAXS grain sizes and specific surfaces of V_2O_5 and V_2O_5 /CeO_2 oxides and obtained insight of grain size distribution within the layer. The grain size and specific surface of all combinations of V/Ce ratio, that is 55 and 38 of atomic percent of V in V/Ce oxide were determined for multiple grazing angles.

GISAXS patterns from V/Ce oxide films are shown in Figure 2. The recorded data are reported in terms of the total scattering vector q that is horizontal (q_y) and vertical (q_z) components. For intercalated V/Ce sample R=2.3±1.6 nm and in the not intercalated sample R=3.3±1.3 nm. Detailed discussion is given in paper by Lučić-Lavčević et al (14).

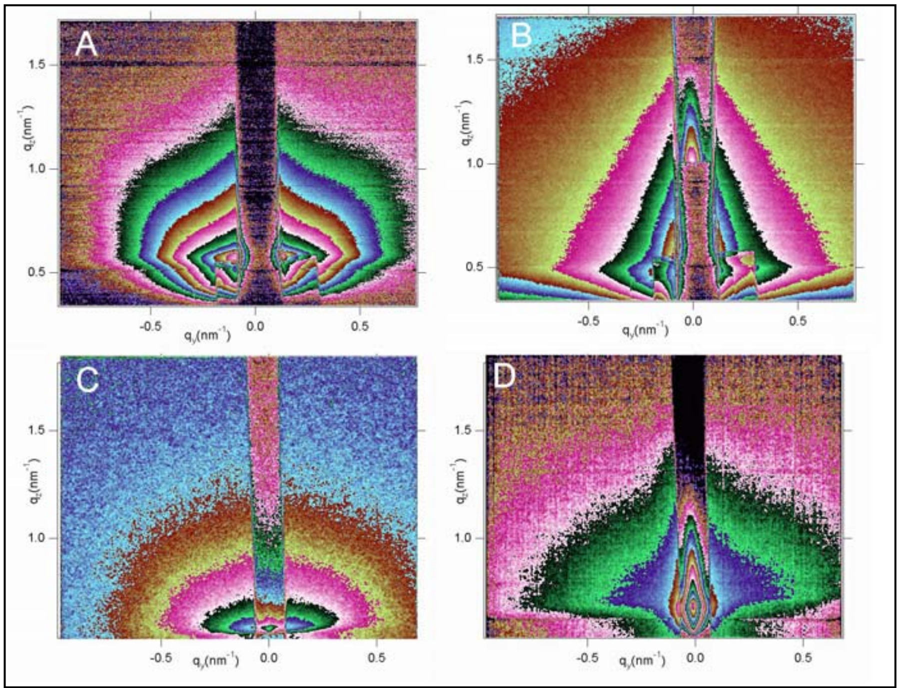

Figure 6. 2d CCD-GISAXS of (A) V_2O_5 and (C) V/Ce oxide and (B) V_2O_5 and (D) V /Ce oxide intercalated with lithium

Schemes of galvanic cells

Schemes of galvanic cells, which were prepared as:

1. $Zn/(PEO)_8ZnCl_2/[V_2O_5\text{-}CeO_2$ (at 38 at. % of V)]; SnO_2:F
2. $Zn/(PEO)_8ZnCl_2$ + 10% P-25 $TiO_2/[V_2O_5\text{-}CeO_2$ (at 38 at. % of V)]; SnO_2:F
3. Zn/(γ-irradiated PEO)$_8$ $ZnCl_2/[V_2O_5\text{-}CeO_2$ (at 38 at. % of V)]; SnO_2:F

By means of electrical measurements, we have shown that polymer electrolyte $(PEO)_8ZnCl_2$ can be combined with $V_2O_5\text{-}CeO_2$ at 38 at.% of V as intercalation cathode in order to obtain all solid-state rechargeable galvanic cell. Further optimisations of electrolyte and electrodes properties are in progress**.** Figures 7 & 8 are showing electrical measurements of characteristics of the cell prepared by scheme 1. Other results for the cells prepared by schematics 2 and 3 were presented in lecture given by Turković (18).

Conclusion

Conclusion 1. The conductivity of $(PEO)_8ZnCl_2$ polyelectrolytes films can be significantly increased by radiation processing of poly(ethylene oxide) and addition of TiO_2 nano-grains. These treatments significantly increased conductivity of polyelectrolytes and lowered temperature of the phase transition.

The results are stimulating for further research of PEO polyelectrolytes and nanocomposites and also gather information on underlying conductivity mechanisms.

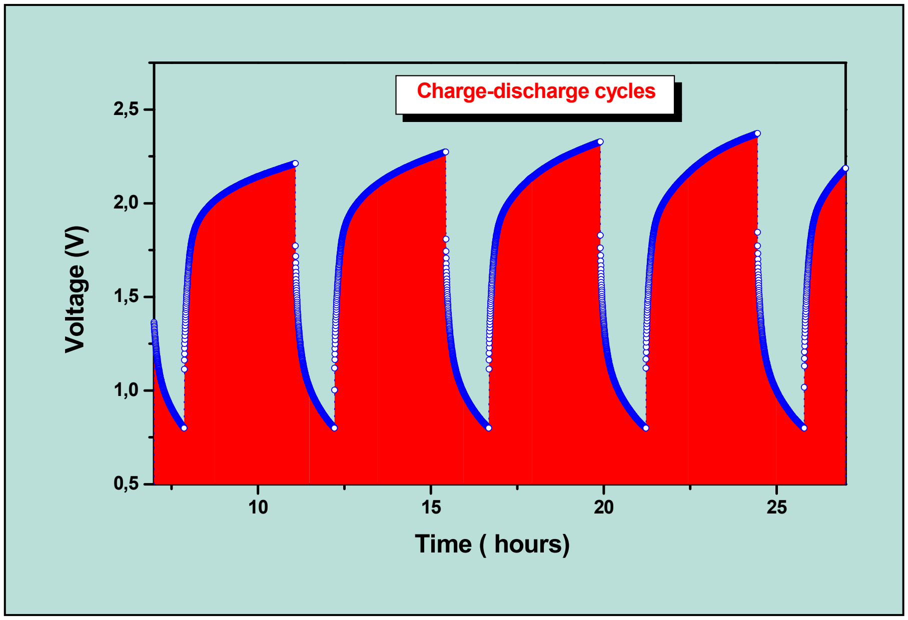

Figure 7. Charge-discharge cycles of cell 1.

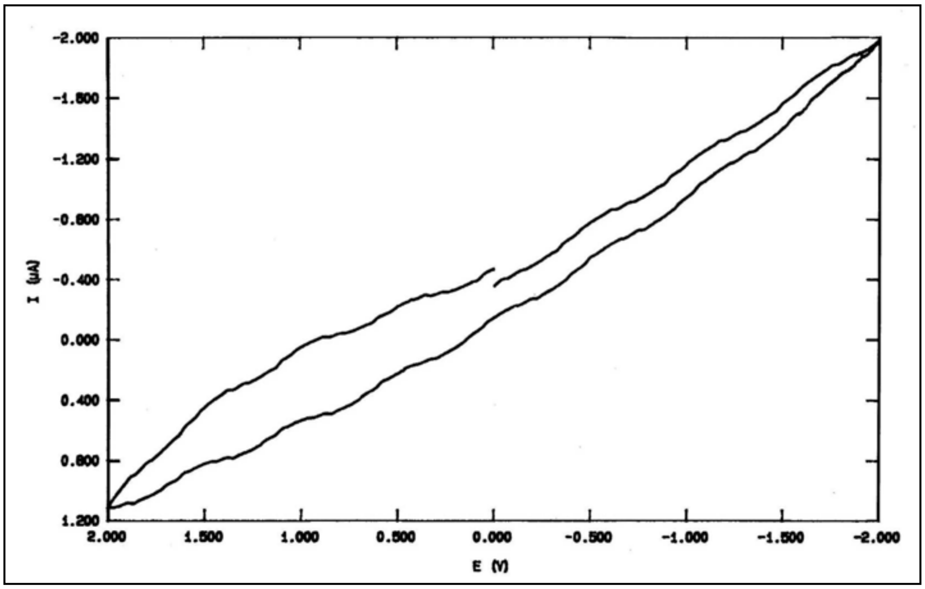

Figure 8. Cyclic voltametry of the cell 1.

Conclusion 2.GISAXS at ELETTRA could be applied for determining grain size and porosity in TiO_2, CeO_2, V_2O_5 and V/Ce oxides on glass substrate as well as for following the process of intercalation of cations into the porous nanostructured films. The morphology obtained by modifying and choosing particular preparation is suitable for application in advanced electrochemical and efficient new solar cells.

Acknowledgments

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