

STRUCTURAL, OPTICAL AND ELECTRICAL STUDIES ON Si-DOPED POLYMER ELECTROLYTES

ŠTUDIJ STRUKTURE, OPTIČNE IN ELEKTRIČNE LASTNOSTI ELEKTROLITOV POLIMEROV, DOPIRANIH S Si

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In this paper we have studied the modification of the structural, optical and electrical properties of a polymer electrolyte film of polyethylene oxide complexed with sodium iodide (PEO:NaI) by doping with Si particles. Structural studies were carried out using Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) measurements. The surface morphology of the polymer electrolyte film doped with Si particles was studied using polarized optical microscopy (POM). For the electrical properties, the electrical conductivity of the films was measured using complex impedance spectroscopy. The ionic transference number measurement (t_{ion}) was carried out and explained in detail to support the electrical conductivity data.

Keywords: polymer electrolyte, FTIR, XRD, POM, ionic conductivity

V tem članku smo preučevali spremembe strukture, optičnih in električnih lastnosti polimernih elektrolitskih plasti polietilen oksida, kompleksiranega z natrijevim iodidom (PEO:NaI) po dopiranju z delci Si. Študij strukture je bil opravljen z uporabo infrardeče spektroskopije s Fourierjevo transformacijo (FTIR) in z rentgensko difrakcijo (XRD). Morfologija površine tanke plasti polimernega elektrolita, dopiranega z delci Si, je bila preučevana s svetlobno mikroskopijo s polarizirano svetlobo (POM). Od električnih lastnosti je bila izmerjena električna prevodnost plasti s kompleksno impedančno spektroskopijo. Izvršeno in razloženo je bilo merjenje številke ionske transference (t_{ion}), ki prispeva k podatkom o električni prevodnosti.

Ključne besede: elektrolit iz polimera, FTIR, XRD, POM, ionska prevodnost

1 INTRODUCTION

Ion-conducting solid polymer electrolytes are arguably the most attractive materials today because of their potential applications in various electrochemical devices, such as dye-sensitized solar cells, supercapacitors, rechargeable batteries, sensors, etc.¹⁻⁷ For electrochemical applications, the electrolytes must be ironically conductive, and at the same time electrode must be compatible with it. Good quality, mechanically strong, semi-crystalline films could be obtained, but unfortunately in most cases the obtainable conductivity is too low (10^{-7} – 10^{-8} S/cm), while for an efficient device we need at least three-to-four orders of magnitude higher conductivity (10^{-3} – 10^{-4} S/cm). To achieve this conductivity value, different approaches have been proposed in the literature, like the use of plasticizers, copolymerization, the formation of blends, changing polymer chain length, composite formation, etc. Of these, composite formation is quite attractive and many composites/blends with various types of dispersoid have been reported in the literature.⁸⁻¹⁰ In this communication, we report an important observation that if semiconducting Si particles are used in forming a composite, a significant conductivity enhancement as well as a structural change can be obtained.

2 EXPERIMENTAL

Before forming the composite, the weight amount of polymer (PEO) and salt (NaI) are taken and films are prepared using a standard solution cast technique. The cation-to-monomer ratio was kept fixed at ≈ 0.065 for all the samples. The different stoichiometric ratios of the semiconducting Si powder (different size) were taken as the dopant to form the composite electrolyte and added to the ion-conducting polymer electrolyte solution. The resultant Si-doped polymer electrolyte solutions were stirred continuously. The final viscous solutions thus obtained were poured into a polypropylene Petri dish. The films, so prepared, were subjected to different characterizations.

To confirm the interaction between the polymer and the semiconductor, Fourier-transform infrared (FTIR) spectra were recorded in the attenuated total reflectance (ATR) mode using a Bruker Tensor 27 spectrometer with a resolution of 4 cm^{-1} in the vibrational frequency range 600 – 3600 cm^{-1} . The X-ray diffraction (XRD, Rigaku D/MAX-RC 12 kW) patterns of the samples were taken with 2θ values ranging from 15° to 65° at a scanning rate of $10^\circ/\text{min}$. The surface morphologies of the composite polymer film were studied with an optical microscope (OM, Leica DM LB) under a cross polarizer.

In order to evaluate the ionic conductivity of the polymer electrolyte film, impedance spectroscopic tech-

niques were used. The conductivities of the polymer films were evaluated from the bulk resistance by ac complex impedance analysis over a frequency range of 100 Hz to 1 MHz. The transference numbers (tion) of the Si-doped polymer electrolyte composite sample are measured using Wagner's polarization method.² In this method the sample is placed between two electrodes in such a way that it minimizes the contact resistance. In an ideal case one of the electrodes is blocking, whereas the other is non-blocking. In the present case we have used stainless-steel electrodes. A dc potential is applied across the sample in such a way that mobile ion species move towards the non-blocking electrode and a small polarization current flows, and finally the sample becomes polarized. The initial total current I_i and the final residual current I_f are used to evaluate the ionic transference number:

$$T_{\text{ion}} = \frac{I_{\text{initial}} - I_{\text{final}}}{I_{\text{initial}}}$$

3 RESULT AND DISCUSSION

3.1 FTIR study

The composite natures of the Si-doped polymer electrolyte and the host polymer electrolyte (PEO:NaI) were confirmed using the FTIR spectra of different samples. **Figure 1** shows the recorded infrared spectra of the PEO:NaI (line 1) and PEO:NaI doped with Si polymer electrolyte films (line 2). Peaks corresponding to various conformations of the polymer chain could be identified.^{11–13} No additional peaks were observed in the FTIR spectra of the Si-doped polymer electrolyte (line 2) other than the host polymer electrolyte (line 1).

This affirms the composite nature of the films. Additionally, the absence of any other peak re-confirms that no chemical reaction takes place between the host and

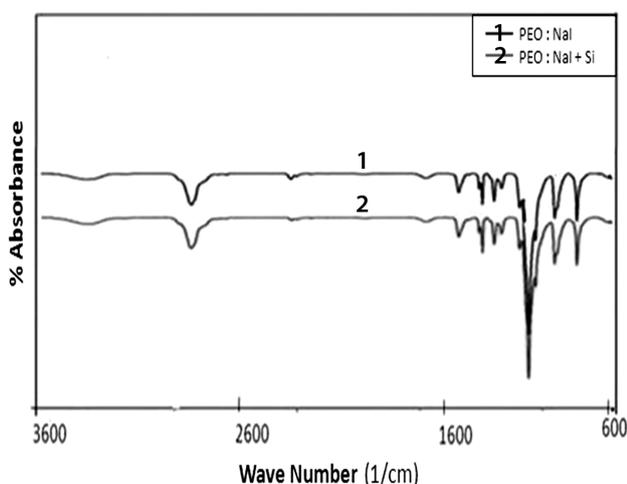


Figure 1: The FTIR spectra of the Si-doped polymer film (line 2) and polymer electrolyte film (PEO:NaI) without Si-doping (line 1)

Slika 1: FTIR-spektra s Si dopirane polimerne plasti (linija 2) in polimerne elektrolitske plasti (PEO:NaI) brez dopiranja s Si (linija 1)

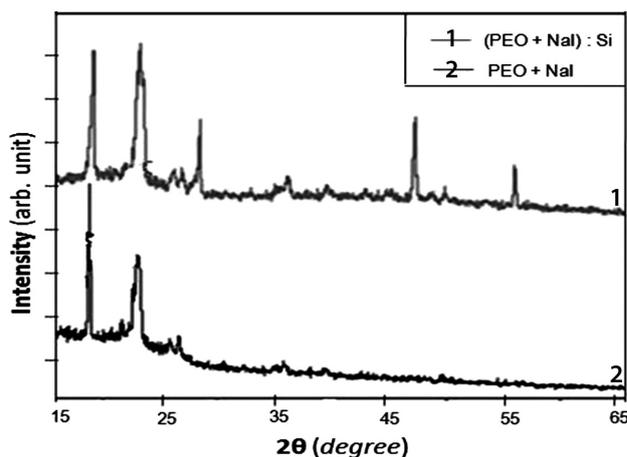


Figure 2: XRD pattern of pure PEO:NaI (line 2) and PEO:NaI doped with Si particles (line 1) polymer electrolyte films

Slika 2: XRD-posnetek čistega PEO:NaI (linija 2) in PEO:NaI, dopiranega z delci Si (linija 1) polimerne elektrolitske plasti

the doped semiconductor. The recorded X-ray diffraction patterns of the Si-doped polymer electrolyte as well as the host polymer electrolyte (without Si-doping) are shown in **Figure 2**. It is well known that the PEO shows a partially crystalline nature, containing a broad hollow between $2\theta = 15^\circ$ and 20° . The Si-doped polymer electrolyte films seems superimposed on this broad hollow.¹⁰ No other peak than the host and the semiconductors clearly confirms the composite nature, as we observed in our FTIR study, discussed earlier.

3.2 Surface study using polarized optical microscopy (POM)

The surface features of polymer electrolyte films with and without Si are further characterized by polarized optical microscopy (POM). **Figure 3** shows the POM photographs of different samples. It was clear that the pure PEO film (**Figure 3a**) shows well the semi-crystalline nature in which large size spherulites are tightly interconnected with each other. Adding NaI into the PEO matrix (**Figure 3b**), the spherulite size becomes small, while the amorphous region (black portion) is

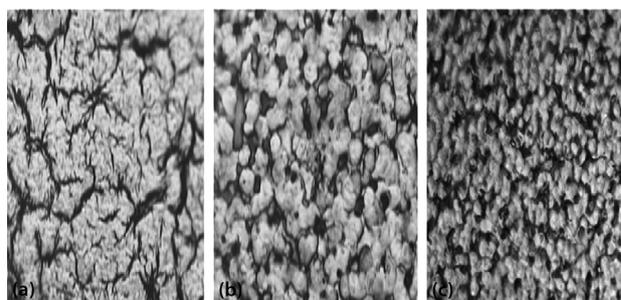


Figure 3: Polarized optical micrographs of: a) pure PEO, b) PEO:NaI and c) Si-doped PEO:NaI polymer electrolyte films

Slika 3: Optični posnetki v polarizirani svetlobi: a) čisti PEO, b) PEO:NaI in c) s Si dopirana PEO:NaI polimerne elektrolitske plasti

increased. It was also noticed that the amorphous region further increases after the Si doping (**Figure 3c**) and Si is preferred to obtain the assembled amorphous region. This shows good agreement with our FTIR and XRD measurements.

3.3 Electrical studies

The complex impedance spectroscopy was used to calculate the bulk electrical conductivity of the polymer electrolyte films.^{14–18} We used pressure-contacted stainless-steel electrodes and connected it with the CH instruments electrochemical workstation (Model CHI604D) with the frequency range 100 Hz to 1 MHz. The electrical conductivity (σ) was evaluated using the formula:

$$\sigma = G \frac{l}{A}$$

where σ is the ionic conductivity, G is the conductance ($G = 1/R_b$ where R_b is the bulk resistance), l is the thickness of the film and A is the area of the polymer sample. The cole-cole plot (complex impedance plot) of a typical sample of PEO + NaI doped with the mass fraction 10 % of Si is shown in **Figure 4**.

The calculated ionic conductivity values are plotted in **Figure 5**. **Figure 5** shows the conductivity vs. composition plot of Si-doped PEO:NaI polymer electrolyte films calculated from various impedance plots. Since the PEO shows a very low conductivity at room temperature ($10^{-9} \text{ S cm}^{-1}$), we have added a small amount of NaI to improve its conductivity. It is clear from the figure that the conductivity increases with increasing Si concentration and the conductivity maxima obtained at the mass fraction of 10 % Si concentration with conductivity value of $4.4 \cdot 10^{-6} \text{ S cm}^{-1}$. This enhancement in conductivity is attributed to the enhancement in the amorphous region by doping with Si particles, which is clearly affirmed by our POM data, discussed earlier.

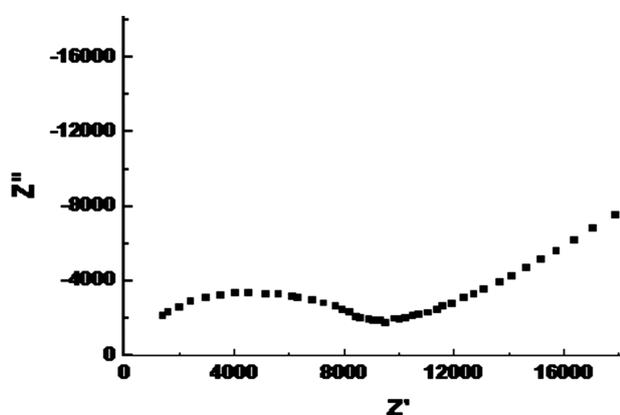


Figure 4: Cole-cole plot of PEO:NaI + 10 % Si polymer electrolyte system

Slika 4: Cole-cole diagram PEO:NaI + 10 % Si sistema elektrolitskega polimera

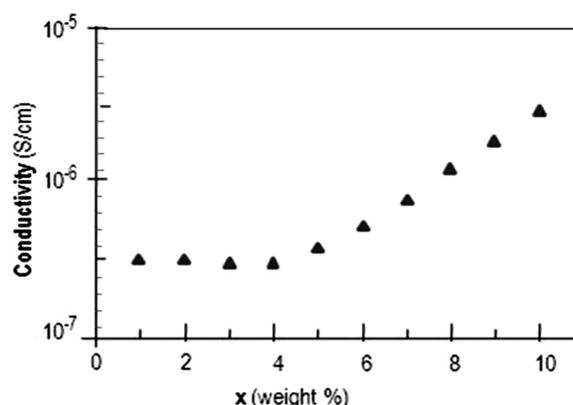


Figure 5: Ionic conductivity (σ) vs. concentration of NaI plot in Si-doped PEO:NaI polymer electrolyte system

Slika 5: Ionska prevodnost (σ) v odvisnosti od koncentracije NaI v sistemu s Si dopiranega PEO:NaI elektrolitskega polimera

3.4 Ionic transference number measurement

The total ionic transference numbers of the Si-doped polymer electrolyte samples are calculated using Wagner's polarization method. **Figure 6** shows the variation of the current with the time plot for PEO:NaI + 8 % Si composite polymer electrolyte film. It can be observed that the current initially decreases rapidly as the time increases. The initial current is due to ionic behaviour, but after a short time the sample becomes polarized and the current is decreased due to the lack of ions. Finally, there are no ions, but a very small number of electrons are still being present inside the sample, which are responsible for the residual current. The transference number calculated in the present system is 0.99, which shows that the system is mostly due to ionic behaviour and is a good candidate for a solid electrolyte.

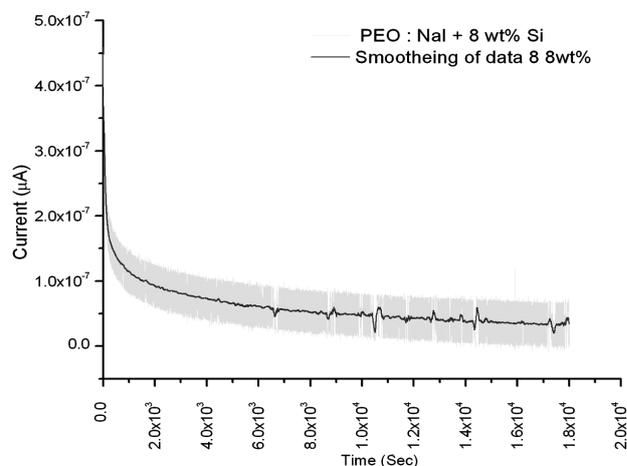


Figure 6: Time vs. current plot for PEO:NaI + 8 % Si composite polymer electrolyte

Slika 6: Čas v odvisnosti od toka za kompozitni polimerni elektrolit PEO:NaI z masnim deležem 8 % Si

4 CONCLUSIONS

A composite polymer electrolyte based on Si-doped PEO:NaI has been developed and characterized. Electrical conductivity measurements show the enhancement in the electrical conductivity by Si doping. IR as well as XRD affirmed the composite nature of the polymer electrolyte samples. Polarized optical microscopy (POM) confirmed the enhancement in the amorphous region by Si doping, which is a well-known condition for conductivity enhancement. Ionic transference number measurements (T_{ion}) suggest that the developed composite polymer electrolytes are ionic in nature.

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