Ionic conductivity study on electron beam irradiated polyacrylonitrile–polyethylene oxide gel*

Ma Yi-Zhun (马艺准)[a)b)], Pang Li-Long(庞立龙)[a)b)], Zhu Ya-Bin(朱亚滨)[a)b)], Wang Zhi-Guang(王志光)[a)†], and Shen Tie-Long(申铁龙)[a)b)]

[a)] *Institute of Modern Physics, Lanzhou* 730000, *China*

[b)] *Graduate University of Chinese Academy of Sciences, Beijing* 100490, *China*

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Different mass percent polyacrylonitrile (PAN)–polyethylene oxide (PEO) gels were prepared and irradiated by an electron beam (EB) with energy of 1.0 MeV to the dose ranging from 13 kGy to 260 kGy. The gels were analysed by using Fourier transform infrared spectrum, gel fraction and ionic conductivity (IC) measurement. The results show that the gel is crosslinked by EB irradiation, the crosslinking degree rises with the increasing EB irradiation dose (ID) and the mass percents of both PAN and PEO contribute a lot to the crosslinking; in addition, EB irradiation can promote the IC of PAN–PEO gels. There exists an optimum irradiation dose, at which the IC can increase dramatically. The IC changes of the PAN–PEO gels along with ID are divided into three regions: IC rapidly increasing region, IC decreasing region and IC balanced region. The cause of the change can be ascribed to two aspects, gel capturing electron degree and crosslinking degree. By comparing the IC–ID curves of different mass percents of PAN and PEO in gel, we found that PAN plays a more important role for gel IC promotion than PEO, since addition of PAN in gel causes the IC–ID curve sharper, while addition of PEO in gel causes the curve milder.

Keywords: polyacrylonitrile, polyethylene oxide, electron beam irradiation, ionic conductivity

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1. Introduction

In recent years, there has been increasing interest in the research and development of polyacrylonitrile (PAN)–polyethylene oxide (PEO) based electrolytes.[1−3] In most studies, some additives were put into it to promote the mechanical properties of the electrolyte. This leads to the influence factors of the increase of electrolyte, causing some difficulties for analysis and cell industrialization. In order to solve the problem, some scientists have begun adopting electron beam (EB) irradiation technology in fabricating polymer based electrolytes.[4,5] As a rapidly developing technology, EB irradiation by using an industrial electron accelerator has many advantages, such as being simple and also being pollution-free. The obtained research results indicate that EB irradiation can not only promote the mechanical properties[6−8] of some polymers due to gel crosslinking,[9−13] but also improve the electrical conductivity of some polymers,[14] perhaps leading to the efficient promotion of dye-sensitized solar cells.[15−20] However, until now, little research has focused on EB irradiated quasi-solid electrolytes. Thus, we tried to promote the ionic conductivity (IC) of a quasi-solid electrolyte (QS-electrolyte) by using EB irradiation and analysed the relation between the IC and the irradiation dose (ID) of QS-electrolyte.

In the present paper, different mass percent PAN–PEO gels were prepared and irradiated by EB with energy of 1.0 MeV to the dose ranging from 13 kGy to 260 kGy. Then, the irradiated PAN–PEO gels were analysed by means of Fourier transform infrared (FTIR) spectrum, gel fraction and IC measurement. Finally, the results of the analysis are discussed.

2. Experiment

2.1. Synthesis of PAN–PEO gels

The 6.65 g PAN was placed in a beaker filled with 100 mL mixed liquor (EC (ethylene carbonate) 50 mL, PC (propylene carbonate) 50 mL). After stirring at

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†Corresponding author. E-mail: zhgwang@impcas.ac.cn

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80°C until the PAN was fully dissolved, 6.65 g PEO was added into the beaker and was stirred together until also fully dissolved. Then, 1.27 g I_2 and 6.69 g LiI were put into the mixture. After stirring for 2 h, PAN–PEO gel was obtained, which contained 5% PAN and 5% PEO (mass percent). Similarly, we obtained the different PAN–PEO gels listed in Table 1.

Table 1. Mass percent PAN or PEO in PAN–PEO (√ = prepared).

PAN	PEO				
	5%	8%	10%	15%	20%
5%	√	√	√	√	√
8%	√	—	—	—	—
10%	√	—	—	—	—
15%	√	—	—	—	—
20%	√	—	—	—	—

2.2. EB irradiation on PAN–PEO gels

Prepared PAN–PEO gels were pressed to 10 μm thickness gels, and then were irradiated by using 1.0 MeV EB delivered by the EB accelerator at the Institute of Modern Physics, Chinese Academy of Sciences (IMPCAS). The ID was from 13 kGy to 260 kGy. The irradiation parameters were as follows: the scanning speed was 0.15 m^2/s, the scanning current was 15.25 mA and the EB irradiation efficiency of the EB accelerator in IMPCAS was 80%.

2.3. FTIR spectrum

The PAN–PEO gels (before and after irradiation) were dried at 50 °C for 24 h and then were characterized by using FTIR (PerkinElmer).

2.4. Gel fraction

The 2 cm × 2 cm region gels were cut from irradiated PAN–PEO gels and then were dried at 50 °C in a vacuum oven for 24 h until their weights were constants. After weighing by an analytical balance, the gels were washed by liquor (ethanol: DMF = 8:2) for 10 min at 60 °C in an autoclave. Similarly, the washed gels were dried to constant weight at 50 °C in a vacuum oven for 24 h and weighed by an analytical balance. Gel fraction was calculated by using the formula

$$f = W_g/W_0 \times 100\%, \quad (1)$$

where W_g is the weight of dry gel after wash and W_0 is the initial weight of dry gel.

2.5. IC

The IC of the PAN–PEO gels was determined by a Conductivity Testing System DB-6200 made by Leici Company of Shanghai in China. The testing temperature in the present work was all at 298 K.

3. Results and discussion

3.1. IR spectrum of PAN–PEO gels

In Fig. 1, many peaks can be found, including broad peaks from 3678 to 3022 cm^{-1} (stretching vibration bond OH, stretching vibration bond NH, intermolecular hydrogen bond and intramolecular hydrogen bond): narrow peaks at 2950, 2911, 2879 cm^{-1} (stretching vibration bond CH in $–CH_3$, $–CH_2$, –CH), sharp peaks at 2239 cm^{-1} (stretching vibration bond –CN) which come from PAN, narrow peaks at 1638 cm^{-1} (stretching vibration bond C=O and in-plane bending vibration bond NH), narrow peaks at 1456, 1424, 1361 cm^{-1} (in-plane bending vibration bond CH in $–CH_3$, $–CH_2$, –CH), dense peaks at 1274, 1179, 1132 cm^{-1} (stretching vibration bond C–N and stretching vibration bond C–O) and dense peaks from 958 to 515 cm^{-1} (out-plane bending vibration bond of NH, OH and CH).

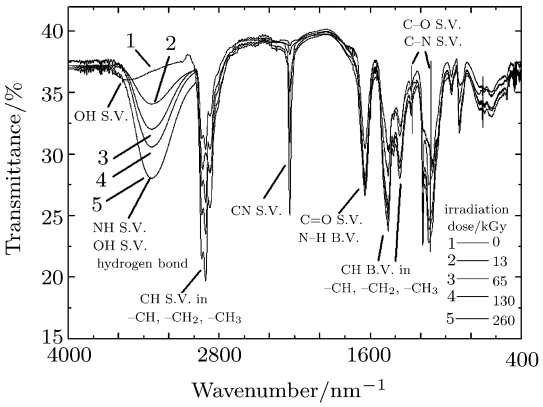


Fig. 1. The IR spectrum of PAN–PEO gels (PAN5%, PEO5%) (S.V. and B.V. represent stretching vibration and bending vibration, respectively.)

Comparing these curves, we find that with the increase of ID of EB, sharp peaks of –CN rapidly decrease. This means that the –CN bond is ruptured by EB irradiation. At the same time, the intensities of

broad peaks of NH, OH stretching vibration, narrow peaks of C–H stretching vibration and dense peaks of C–N, C–O stretching vibration all indicate the ruptured –CN bond changes into C–N, N–H, C–O, C–H, etc., leading to the crosslinking of the gels. Based on the EB effects on polymers,[21−23] these structural changes can be ascribed to EB irradiation on the gels.

3.2. Gel fraction of PAN–PEO gels

From Fig. 2, it is found that gel fraction continuously increases with electron ID. The process can be divided into two portions. One is a gel fraction rapidly rising portion (before 104 kGy), the other is gel fraction slowly rising portion (after 104 kGy). The results are similar to that of the research about some kinds of hydrogels.[24,25] The curves indicate that crosslinking degree of PAN–PEO gel increases with ID.

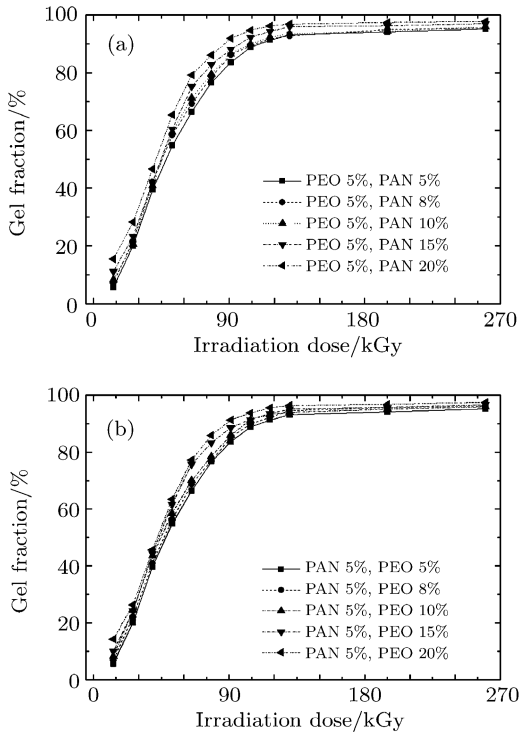


Fig. 2. Gel fraction of PAN–PEO gels: (a) with fixed PEO mass percent, (b) with fixed PAN mass percent.

Furthermore, we obtained crosslinking rate–ID curve as shown in Fig. 3 by differentiating the gel fraction–ID curve. It is observed that the crosslinking rate is high at first, and then gradually falls until its value trends towards zero. In addition, the mass percents of both PAN and PEO contribute a great deal to crosslinking, since the mass percent of the PAN or the PEO is larger, the crosslinking rate of the gel is higher at a certain ID.

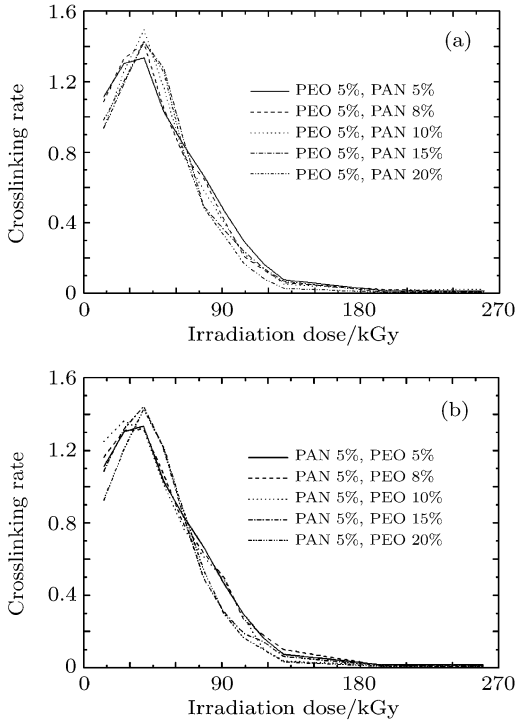


Fig. 3. Crosslinking rate of PAN–PEO gels: (a) with fixed PEO mass percent, (b) with fixed PAN mass percent.

3.3. IC of PAN–PEO gels

3.3.1. EB ID effects on IC of PAN–PEO gels

It is observed from Fig. 4 that the IC of PAN–PEO gels rapidly increases with the increase of ID before 65 kGy, and then gradually decreases with the increase of ID. According to the hypothesis presented by Ying,[14] we can ascribe the increase of IC before 65 kGy to anion formation through electron capturing by gels. Referring to the Nernst–Einstein equation (2) of Ref. [26], we can describe relations between the gel's IC conductivity and the ionic concentration as

$$\sigma = \frac{Nq^2}{kT} D_{\rm c}, \tag{2}$$

where σ is the IC of polymer based gels, k is the Boltzmann constant, T is the testing temperature, $D_{\rm c}$ is the ionic diffusion coefficient, N is the ionic concentration and q is the ionic charge.

During the EB irradiation process, free radicals in gels are produced by EB irradiation,[27,28] and more and more free radicals capture electrons and become transmission ions, which leads to the increase of ionic concentration (N) in Eq. (2). In addition, the ionic charge also increases because free radicals continuously capture electron until saturation, which leads

to the rise of ionic charge (q). Under the influence of the two aspects, IC rapidly increases. However, when ID exceeds a certain dose, free radicals begin to reduce due to the enhancing crosslinking degree, which causes a decline of ionic concentration, and causes a drop of IC (σ). In addition, the enhancement of the crosslinking degree with ID causes a smaller molecular network, which reduces the free volume in gels. Since the smaller network limits ion transmission, the ionic diffusion coefficient (D_c) declines, leading to the lowering of IC. The effects can be more clearly described by[29]

$$\sigma = \sigma_1 \exp\left[-\left(\frac{rV'}{V_f} + \frac{W_1 + \frac{W'}{2\varepsilon}}{kT}\right)\right], \qquad (3)$$

where σ_1 is a constant dependent on electric field, r is the free volume overlap correction factor, V' is the necessary volume for ionic migration, V_f is the free volume, W_1 is the activation energy for ionic migration, W' is the ionic thermal dissociation energy and ε is the dielectric constant. Obviously, crosslinking induced by EB irradiation lessens the free volume (V_f) in the gels, causing the decrease of IC.

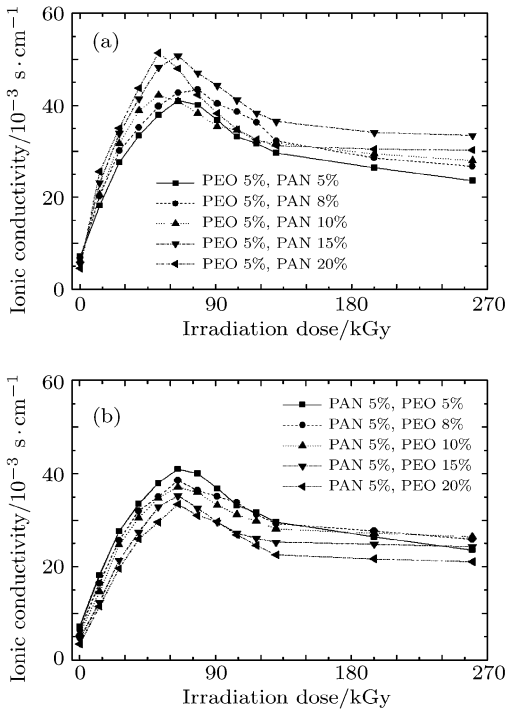


Fig. 4. The change of IC of PAN–PEO gels with the ID of EB: (a) with fixed PEO mass percent, (b) with fixed PAN mass percent.

Generally speaking, the change of IC–ID curve can be divided into three regions. The first region is an IC rapidly increasing region. In this period, the electron capture in gels plays a dominant role (0–65 kGy), N and q rapidly increase, leading to the high increase rate of IC. The second region is IC decreasing region. In this region, the electron capturing degree of the gel is saturated. The ionic charges remain constant, but the crosslinking rate of the gels is still high. This causes a decrease of free ionic concentration and ionic diffusion coefficient. The decreases of N and D_c result in the falling down of IC (65–104 kGy). The third region is an IC balanced region. In this region, not only the capturing electron degree of the gel but also the crosslinking degree of gel are saturated. The very slow crosslinking rate, which can be found in gel fraction–ID curve in Fig. 2, causes the slow decrease of ionic concentration and ionic diffusion coefficient (104–260 kGy). Accordingly, there exists an optimum ID, at which the value of the IC is the highest.

3.3.2. PAN and PEO ratio effects on IC of PAN–PEO gels

From Fig. 5 (a), we can see that when adding more polymers in the gel (PAN5% and PEO5%), whether adding PAN or PEO, the IC of the gel decreases. The result is consistent with that of some other studies.[30–32] Linearly fitting the results in Fig. 5(a), we obtained Fig. 5(b) and discovered that while adding equal amounts of PEO and PAN into the gel (PAN5%, PEO5%), the IC of the added PEO gels decreases faster than that of the added PAN gels. This phenomena can be ascribed to the higher electric resistance of PEO.

As depicted in Fig. 6, the IC of PAN–PEO gels is markedly increased in rapidly increasing IC regions (0–65 kGy) because of the high slope value of IC. The higher the mass percent of PAN in PAN–PEO gels is, the higher the slope value of IC is. That is to say, under the condition that the total mass percent of the polymer is in the range of from 5% to 25%, the increase of PAN mass percent is beneficial for the rise of the IC of PAN–PEO gels. In the region of decreasing IC (65–104 kGy), we find that the more PAN there is in gels, the higher the decreasing rate of IC is. In the balanced region, the mass percents of PAN and PEO both slightly affect the increasing rate of IC of the gel, for the rate is close to zero.

To sum up, PAN plays a more important role in PAN–PEO gel than PEO for the increase of IC. The more PAN is in the gel, the sharper change of IC can be shown, while the more PEO is in the gel, the smaller change of IC can be found.

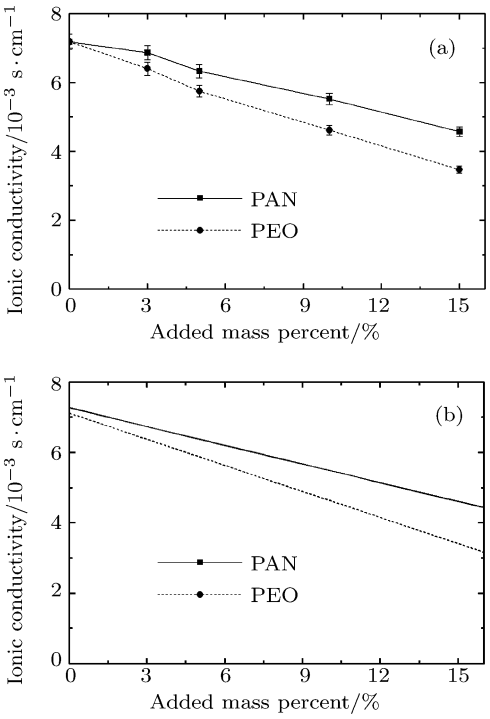


Fig. 5. The change of IC with added mass percent of PAN or PEO into un-irradiated gels of 5%PAN and 5%PEO. (a) Influence of increasing net PEO/PAN mass percent on IC, (b) the linear fitting of (a).

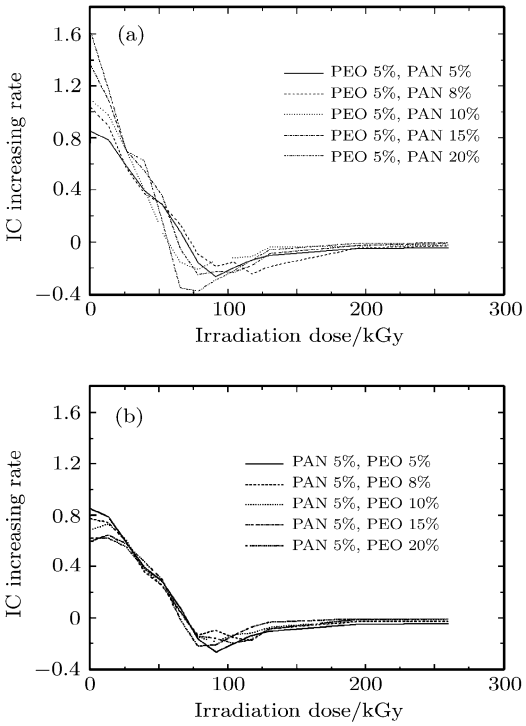


Fig. 6. The increasing rate of IC of PAN–PEO gel: (a) with fixed PEO mass percent, (b) with fixed PAN mass percent.

4. Conclusions

According to the experimental results and the analysis mentioned above, the following conclusions can be drawn:

1) From FTIR spectrum analysis, EB irradiation can lead to crosslinking of PAN–PEO gels.

2) It is indicated from the gel fraction–ID curve that the crosslinking degree increases with the increasing ID of EB irradiation dose. The crosslinking rate is as high when ID is low, and gradually falls to zero when ID is high. The mass percents of both PAN and PEO contribute a great deal to the crosslinking degree, since the higher mass percent of the PAN or PEO is in the gel, the higher crosslinking rate the gel possesses at a certain ID.

3) The EB irradiation increases the IC of the PAN–PEO gel in comparison with the un-irradiated gels. There is an optimum ID, at which the IC of the PAN–PEO gel is the highest. The change of the IC of PAN–PEO gel with the ID can be divided into three parts: IC rapidly increasing region, IC decreasing region and IC balanced region. The cause of the change can be ascribed to two aspects, gel capturing electron degree and crosslinking degree.

4) By comparing the IC–ID curves of different mass percents of PAN and PEO in the gel, we find that more PAN in the gel leads to a sharper IC–ID curve, while more PEO in the gel causes a more gentle curve, which indicates that PAN plays a more important role than PEO for the increase of IC of the PAN–PEO gel.

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