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Polypyrrole conductive films obtained electrochemically on polycarbonate coated platinum electrodes

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Abstract

Polypyrrole is prepared by electrochemical polymerization of pyrrole on platinum electrode coated polycarbonate (PC) .This method produced a homogeneous conducting polymer with electrical conductivity, 6 S/cm .The electrical conductivity is measured by four-probe method The electrical conductivity is measured as a function of current density, concentration of supporting electrolyte and time of polymerization .The effect of ammonia solution on the conducting is also investigated. ,

Introduction

can be Polymer with conjugated л-electron (i.e system with C = C conjugated double bond), convered to conducting polymer by reduction or oxidation reaction (called doping)[1]. Conducting polymers have attracted great attention because of their applications , such as electronic elements [2], rechargeable batteries[3], optical switching elements [4]and sensors[5]Polypyrrole is one of these conducting polymers.It is easily prepared electrochemically,Perhaps due to the very low oxidation potential of pyrrole monomer .The electrical conductivity of poly pyrrole varies between (10 -100)S/cm as reported by several authors[6,7,8].But conducting polymers have been plagued in the past which problems associated with poor mechanical properties [7].It was found that the electrochemical polymerization of pyrrole proceeds on electrode whose surface is coated with ordinary insulating

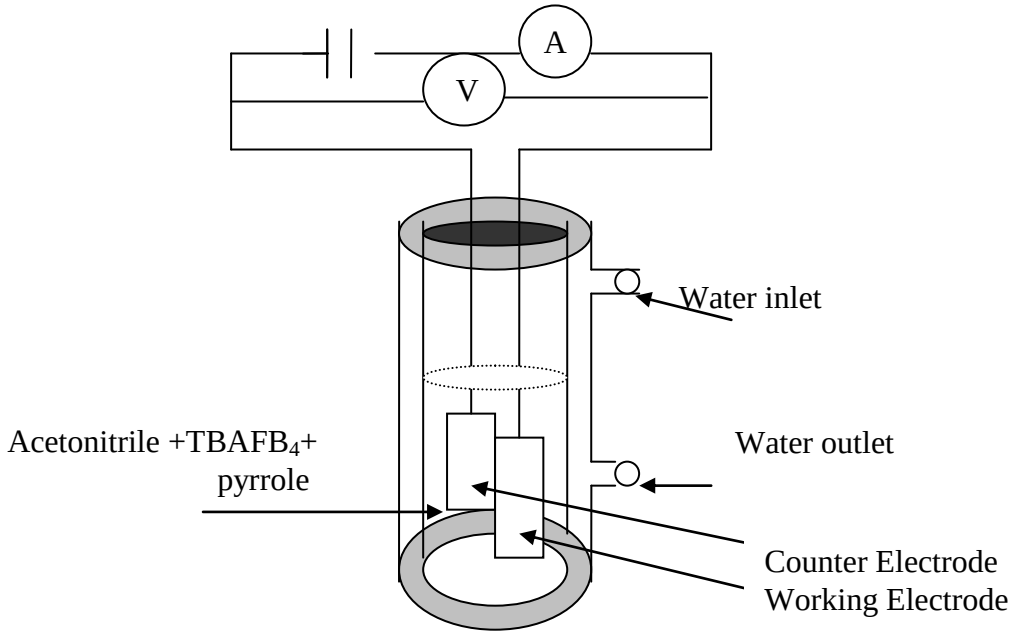
polymer film such as polypyrrole composites with poly(tetrafloroethylene), poly(vinylchloride)and Poly(vinyl alcohol)[8,9,14] The mechanism of polymerization of the films which is prepared by electrochemical polymerization of pyrrole in electrochemical cell[10] , in the present work polypyrrole/polycarbonate (PPy/PC) is prepared by electrochemical polymerization of pyrrole on stainless steel electrode coated with PC .The electrical properties of doped and undoped films were also investigated .

Experimental

Polypyrrole ppy, blended with polycarbonate(PC is prepared by electrochemical polymerization. PC(moleculer weight M_w=60000g/mol,thichness 15 µm,density 1.2 g/ml,T_g=150^oC)

The PC -coated electrode was prepared by dropping 0 .6 ml of 1% PC in chloroform on both surfaces of the Pt foil(2x3)cm^2 electrode and evaporating The solvent .the thickness of the PC coating is approximately 15 µm. which is used as working electrode in the electrochemical cell .The counter electrode is platinum electrode . These electrodes are connected to power supply as shown in Fig.1[9] The distance between the electrodes is 0.4 cm .During the polymerization the pyrrole blend with PC and forms PPy/PC film Preliminary studies revealed that this PC thickness was suitable for the Diffusion of the monomers to the electrode surface and to produce a free-standing and durable conductive polymer film .The amount of PC coated on the electrode was determined from the weight of the electrode before and after the coating process. The PC-coated electrode was then used in the electrolysis of pyrrole in a solution of 0.3 M pyrrole and 0.05 M ($TBAFB_4$) tetrabutylammonium tetrafluoroborate as supporting electrolyte at a potential of 3 V . The PPy/PC coated electrode taken from the cell .This film could be easily stripped from platinum electrode was washed with water and acetonitrile, dried in vacuo at 50 ^oC and weighted .The amount of ppy in the film structure was determined from the weight of the electrode coating before and after electrochemical process. PPy/PC films ,containing varying amounts of ppy , were obtained by changing the electrolysis time .The

conductivity of the films was determined by the four probe technique.Different current density from (0.4 - 8) mA/cm^2 and concentration of supporting electrolyte ($TBABF_4$) from (0.001 to 0.3) mol/L Were investigated in order to choose the proper current density for polymerization and the concentration of $TBABF_4$ that gives a good quality films.The best quality films were obtain at current density 3 mA/cm^2 With solution mixture at 0.1M $TBABF_4$ and 0.2 M pyrrole in acetonitrile was used as a solvent . The electrolysis of pyrrole in acetonitrile The temperature of mixture is at room temperature.The thickness of (PPy/PC) film was about 64μm. Then washed with tetrahydrofuran solution The electrical conductivity ,σ,was measured by four-probe method [10] at room temperature the thickness of the films is measured by using Faradys law[11]. .



Figure(1) The electrochememical polymerization cell.

Results and Discussion

The electrical conductivity for each sample ,σ, is calculated with follwing eq[12]

$$\sigma(S/cm) = \frac{\ln 2}{\pi d}\left(\frac{I}{V}\right)$$

where d is the thicknes of the films which is in the range (40 - 65) μm, (I) is the current between the two probes and (V) is the voltage between the other two probes .

The quality of the films was examined by measuring the conductivity, σ,as a function of current density ,J, and concentration of the supporting electrolyte

$TBABF_4$.(Fig.2)shows the variation of conductivity with current density. The optimum current density was found to be 1.9 mA/cm^2This was carried out by using 0.3 M $TBABF_4$ as supporting electrolyte and 0 .2 M pyrrole monomer in acetonitrale.The maximum value of conductivity for PPy/PC is 6.2 S/cm .at low currentdensity values, the conductivity was low. . This can be attributed to the fact that the current density is not enough to completly process of doping for PPy/PC with BF_4 anion . while current density makes high values of current density gave low conductivity because the polymerization too fast , so that some polymer fragments fail in the solution [10].

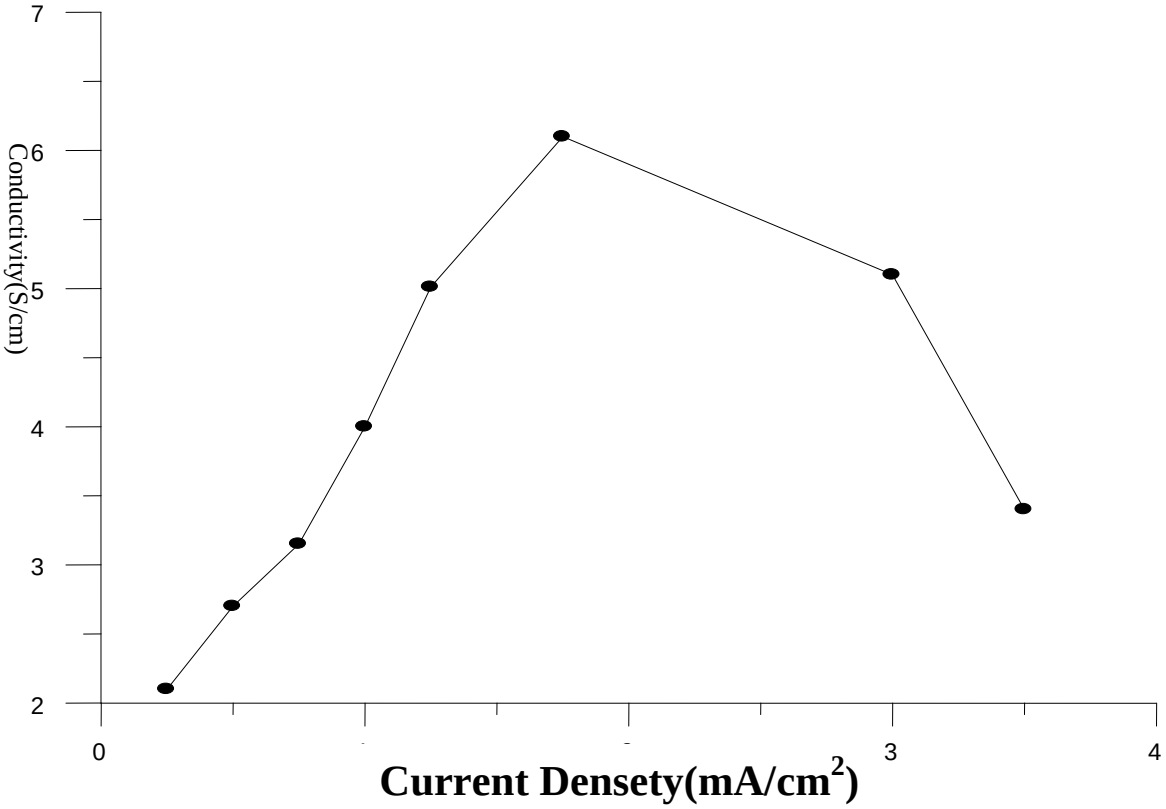


Fig.2 The conductivity as a function of current density.

Fig 3, shows the dependence of conductivity on $TBABF_4$ concentration. The saturatation in conductivity observed at concentration larger than 0.2 mol/L,

Because the conductivity depends on the degree of oxidation or reduction

In л-electron system and which is determined by number of conjugate carbon[12]

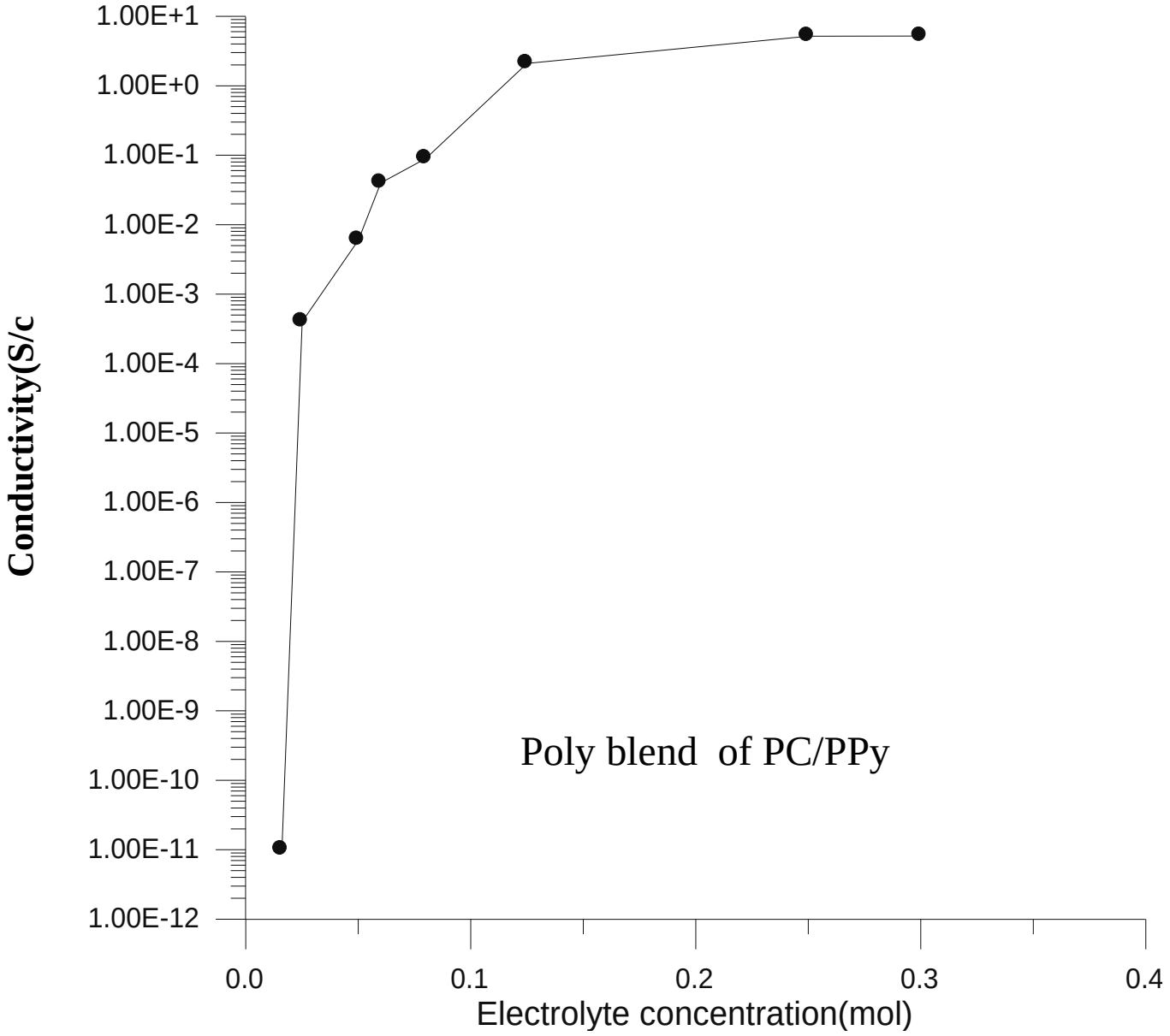


Fig.3 The conductivity as a function of concentration of $TBABF_4$.

The effect of polymerization time on the conductivity is shown in Fig.4, which shows the best time of polymerization is 9 min.

0 11 20 25 40 46 60 70 80 100 PPY(%)

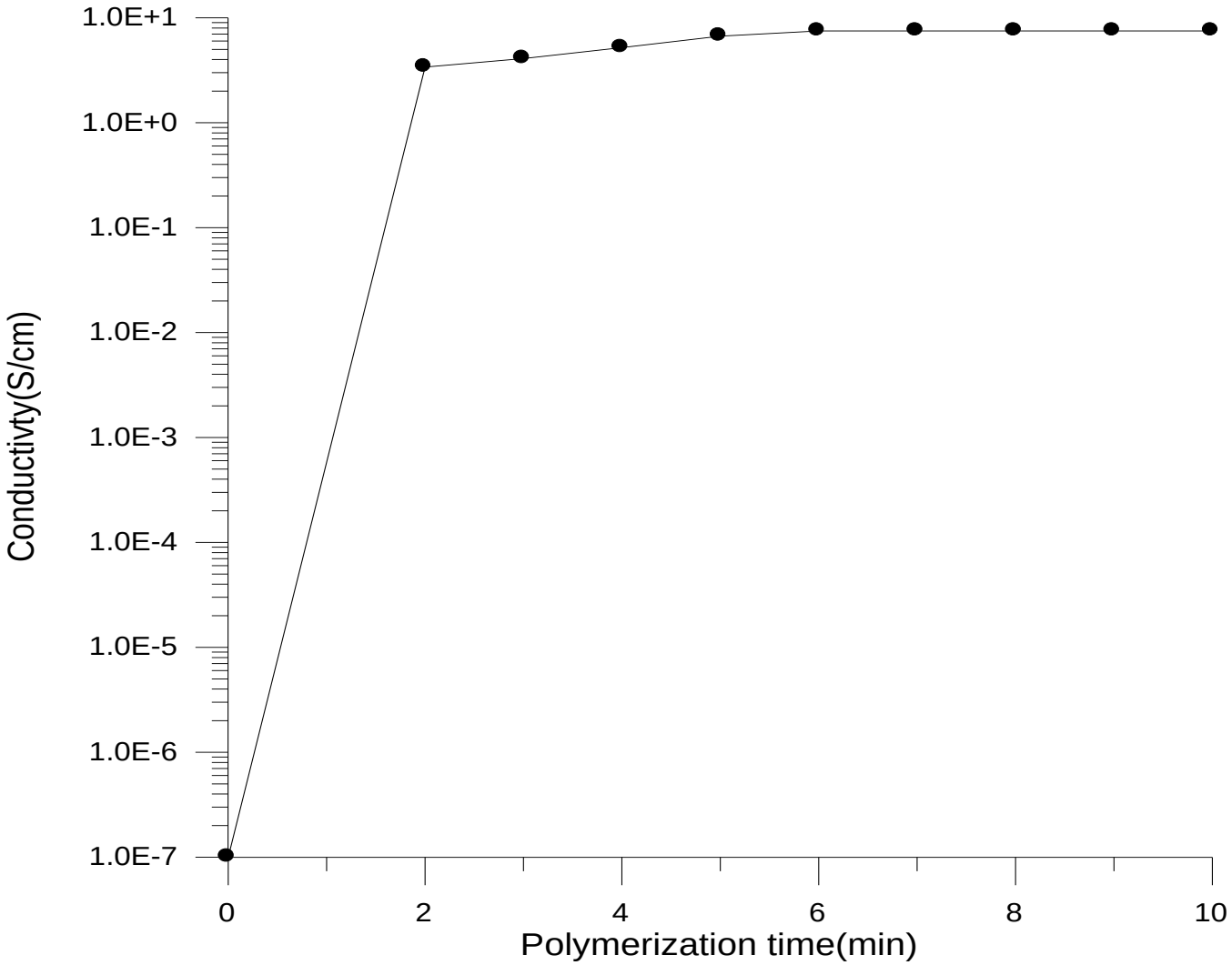


Fig.4 The conductivity as a function of polymerization time

and conductiviyy of PPy/PC films containing different a mounts of ppy were prepared by changing the polymerization time .The change of the electrical conductivity of these films depending upon their PPy content is shown in Fig.4The conductivity of PPy/PC films increased with the amount of PPy included , and the conductivity of the films containing 80% PPy or more remained almost constant at 6 Scm^{-1} . This value corresponds to the conductivity of pure PPy[15]

The conductivity of undoped film was measured after immersing the PPy/PC in ammonia solution .Fig.5 shows the conductivity of PPy/PC as a function of immersion time.The film causes rapid decrease in its conductivity,and reaches a value corresponding to that of undoped PPy (10^{-3}S/cm) and remains almost constant after immersed in ammonia solution This can be explained in terms of compensation process[12]. The conductivity of doped film is higher than for the undoped film (10^{-3}S/cm). This may be attributed to the redox process is not completely [13]

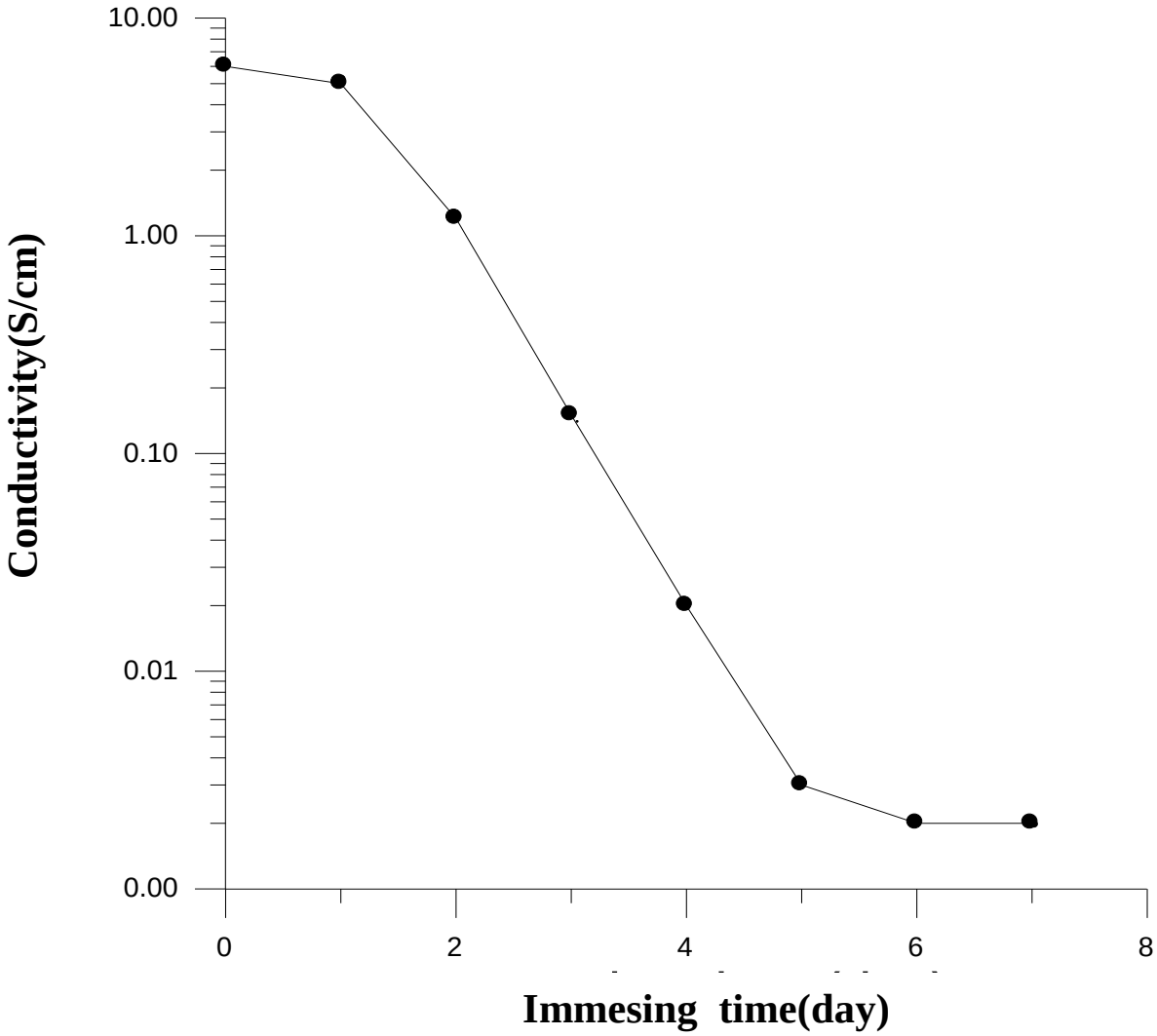


Fig.5 The conductivity as a function of immersing time in ammonia solution .

تحضير سبائك بوليمرية موصلة من البولي بايرول والبولي كاربونيت

(PPy/PC) بطريقة البلمرة الكهروكيميائية ودراسة خصائصها الانتقالية

جامعة ذي قار/كلية العلوم /قسم الفيزياء

م. سامر مهدي المالكي

المستخلص

حضرت اغشية بوليمرية من المركبات الحلقية (البايرول) المتعددة يمكن بلمرتها بالأكسدة الكهروكيميائية في محلول يتكون من الالكتروليت الساند ومن المونيمرات العضوية الحلقية المتعددة هو ا لبايرول حيث يتم التشويب موقعيا اثناء عملية البلمرة الكهروكيميائية لينتج غشاء متجانس منتظم موصل.و تم تحضير سبائك بوليمرية موصلة من البوليمر الموصل البوليبايرول المشوب $TBABF_4$ والبوليمر العازل بولي فينايل الكلور PC بطريقة البلمرة الكهروكيميائية حيث تمت بلمرة البايرول موقعيا على قطب من البلاتين المغطى بالبوليمر العازل PC درست الظروف المثلى لتحضير سبيكة PPY/PC من خلال السيطرة على فولتية البلمرةوتركيز المحلول الالكتروليتي وكثافة تيار البلمر ة والزمن ألازم للبلمرة .استخدمت طريقة المجسات الأربعة Four probe method في قياس التوصيلية الكهربائية للسبائك المحضرة حيث تم الحصول على سبيكة بوليمرية بلغة توصيليتها إلى (6 S/cm) كذلك درست إمكانية تحويل السبيكة البوليمرية PPY/PC من بوليمر موصل إلى عازل وبالعكس وذلك عن طريق غمرها بسائل الامونيا ودرست تأثير زمن الغطس على التوصيلية الكهربائية.

Conclusion

Pyrrole gave homogeneous and free-standing films on a PC -coated Pt electrode In organic media and the optimum condition for good quality films of PPy/PC was prepared by electrochemical polymerization at current density 1.9 mA/cm^2 , $TBABF_4$ concentration 0.3 mol/L and the polymerization time at 9 min .The doped films of PPy/PC can be changed in to undoped films when immersed in ammonia solution .The conductivity of these films drop from 6.2 to 10^{-3} S/cm when the immersing time is about 7 day .

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