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STUDIES REGARDING ELECTROCHEMICAL POLYMERIZATION OF ANILINE IN IONIC LIQUID AND POLYMER PROPERTIES

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Lichidul ionic pe bază de clorură de colina şi uree (ChCl-urea) a fost folosit ca solvent şi electrolit pentru polimerizarea electrochimică a anilinei pe electrod de platină prin voltametrie ciclică (CV), experimente realizate la temperatura camerei. Oxidarea anilinei începe la 1.2-1.3 V vs electrodul de quasireferintă de argint, iar curentul de pic anodic creşte cu creşterea numărului de cicluri. Electrozii modificaţi cu polianilină (PANI) prezintă activitate electrochimică în soluţia de lichid ionic. Pentru comparaţie, curba CV pe electrod de Pt neacoperit cu polimer în amestecul ChCl-uree are o densitate de curent scăzută pe acelaşi domeniu de potenţial. Spectrele de impedanţă electrochimică prezintă o dreaptă la frecvenţe mici (răspuns difuziv), în timp ce la frecvenţe ridicate se înregistrează semicercuri (răspuns capacitiv), ceea ce înseamnă că procesul de oxidare se află sub control de difuzie şi repectiv cinetic.

Choline chloride-urea ionic liquid (ChCl-urea) has been used as solvent and electrolyte for the electrochemical polymerization of aniline on platinum electrode by cyclic voltammetry (CV). The tests were performed at room temperature. The oxidation of aniline starts at 1.2-1.3 V vs Ag quasireference electrode and the anodic peak current increases with increasing number of scans. The electrode modified with polyaniline (PANI) has electrochemical activity in ionic liquid solution. For comparison, a CV curve for the non-covered with polymer Pt electrode in ChCl-urea mixture reveals low current density over the same range of potential. The electrochemical impedance spectra exhibit a straight line at low frequency (diffusive response) while semicircles (capacitive response) at high frequency are recorded, which means that the oxidation process is diffusion and kinetic controlled, respectively.

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1. Introduction

Ionic liquids and conducting polymers are two of the most interesting research areas from the last decade. Conducting polymers are organic materials that can display electronic, magnetic and optical properties similar to metals, but also having the mechanical properties and low density of a polymer. They have the potential to allow the design and fabrication of a vast number of electrochemical devices including photovoltaics, batteries, chemical sensors, supercapacitors, conducting textiles, electrochromic devices and electromechanical actuators [1-8]. In addition, these materials have a significant impact in the major area on new biomedical processes such as controlled neural growth involved in spinal regeneration.

The term *ionic liquids* was given to distinguish the low temperature ionic liquids from the high temperature melts that are composed predominantly of inorganic ions. Several industrial applications of ionic liquids were already tested and these are as diverse as fuel desulfurization and precious metal processing [9]. Among other polymers, polyaniline (PANI) is a conducting polymeric material which can be synthesized either chemically or electrochemically. It has many applications in various domains. PANI belongs to a group of conducting polymers prepared by the electrochemical oxidation and simultaneous polymerization of monomer that reacts at the anode of an electrochemical cell. The electrochemical preparation and characterization of polyaniline are commonly used [10, 11].

The potential benefits of using conducting polymer in devices have been investigated by a number of authors in recent years [1-9], for applications such as actuators, supercapacitors, electrochromic devices and solar cells, with significant improvements in lifetime and device performance reported. The use of ionic liquids is often prompted by safety and environmental considerations where negligible volatility and nonflammability makes them ideal replacements for more toxic molecular organic solvents and, importantly, overcomes the problem of solvent evaporation that exists with the long-term use of volatile solvents in electrochemical applications. Parameters such as viscosity and electrical conductivity, the high ionic concentration compared to conventional solvent/electrolyte systems, as well as the nature of the cation and anion themselves, may all influence the polymer properties such as structure, doping level, growth rate, growth mechanism, morphology, conductivity etc.

Polyaniline synthesis in ionic liquids has also been investigated. Miao et *al* prepared polyaniline networks in 1-hexadecyl-3-methylimidazolium chloride [12], Innis et *al* synthesized polyaniline in 1-ethyl- 3-methylimidazolium bifluoromethanesulphone imide [13]. However, we consider that the polyaniline synthesis is still a topic of interest, especially regarding the use of alternative ionic liquids. For instance, the synthesis of polyaniline in the ChCl-urea ionic liquid was not studied, yet. The aim of the present research is the study of electrochemical polymerization of aniline on platinum substrate using choline chloride based ionic liquids. We also present the influences of some parameters on the properties of obtained polymer.

2. Experimental

The solutions were prepared from analytical grade reagents; choline chloride, urea (Aldrich) and aniline (Merck) were used as received. Choline chloride-urea ionic liquid was formed by mixing the two components in the molar ratios (1:1 and 1:2) and heated at 70^0C until a colourless liquid is obtained. An aqueous solution containing 0.5 M H_2SO_4 + 0.5 M aniline was also prepared for polyaniline synthesis.

The electrochemical cell was a single compartment glass cell with three electrodes; a platinum foil (1 cm^2) was used as working electrode, a Pt plate was the auxiliary electrode and a silver wire immersed in the working ionic liquid was the quasi reference electrode. The electrochemical synthesis of polyaniline (PANI) was accomplished by cyclic voltammetry. The transfer solution in which the properties of polyaniline film were investigated was the same ionic liquids without aniline addition.

The studies were accomplished using a potentiostat/galvanostat Voltalab 40 Radiometer Analytical coupled to a computer equipped with VoltaMaster 4.0 software for data aquisition and processing. The obtained polyaniline film was characterized using two electrochemical techniques: cyclic voltammetry and electrochemical impedance spectroscopy (EIS). Cyclic voltammograms (CVs) were recorded with various scan rates up to 100 mV/s. EIS measurements were carried out applying an a.c. voltage of 10 mV amplitude and the frequencies in the range 100kHz - 50mHz. All tests were performed at room temperature (25^0C).

3. Results and Discussions

3.1. Electrochemical polymerization of aniline

Preliminary studies were made for aniline polymerization in choline chloride and urea mixtures by changing the molar ratio of the two ionic liquid components. The potential sweep is started from the lower potential limit (cathodic limit) towards anodic direction and back. The recorded voltammograms show a single well-defined anodic peak and one corresponding cathodic peak.

The 20th cycle of the cyclic voltammograms of aniline polymerization in ionic liquids at 25^{0}C is presented in Fig. 1. It can be seen from this figure that in ChCl:urea 1:1 molar ratio mixture the current density is lower on both anodic and cathodic branches; however, the anodic and cathodic peaks recorded in 1:1 molar ratio are better defined than for 1:2 molar ratio mixture. In both cases we noticed that the successive voltammograms show an increase of current density with cycling, meaning that the polymer thickness is increasing with increasing cycle number.

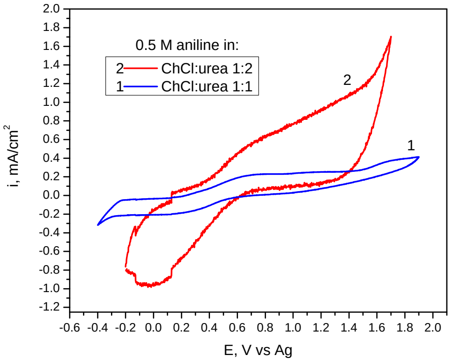

Fig. 1. Comparative voltammograms (20th cycle) on Pt electrode in 0.5 M aniline containing ChCl:urea 1:1 and 1:2 mixtures, scan rate 50 mV/s, temperature 25^{0}C

The current density along the cyclic voltammograms increases with increasing scan rate in all cases; an example is given for the current density in ChCl:urea (1:2) + 0.5 M aniline solution (Fig. 2).

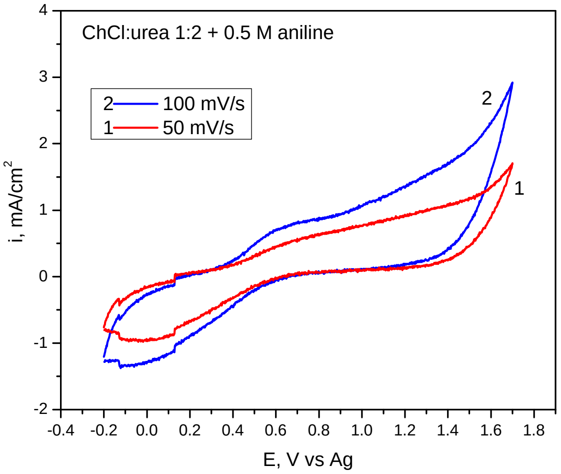

Fig. 2. Aniline polymerization on Pt electrode in ChCl:urea (1:2) + 0.5 M aniline, 25^{0}C; the 20th cycle with different scan rates: 50 mV/s (1) and 100 mV/s (2)

The influence of aniline concentration was also studied in both ionic liquids. The cyclic voltammograms recorded on platinum electrode for ChCl:urea 1:1 ionic liquid blank or containing different concentrations of aniline are presented in Fig. 3. As can be seen in this figure, during the electropolymerization in choline chloride-urea 1:1, the higher the concentration of aniline, the greater the current density. Also, the oxidation potential is more positively for the anodic peak at higher concentration of aniline.

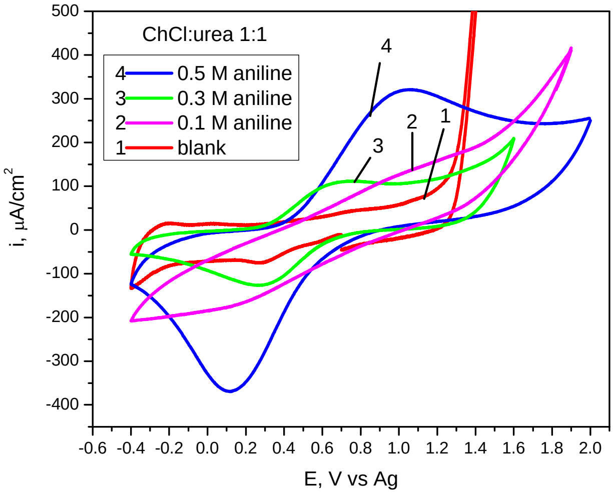

Fig. 3. Cyclic voltammograms on Pt electrode of pure choline chloride-urea 1:1 (1) and with aniline addition of various concentrations: (2) - 0.1; (3) - 0.3 and (4) - 0.5 M aniline, respectively. Scan rate 50 mV/s, temperature 25^0C

The polymer oxidation and reduction peaks show an increase in current with successive cycles indicating the deposition of increasing amounts of electroactive polymer. By alternating the potential sweep (anodic and cathodic) repeatedly a partial dissolution and then a new growth of the polymeric film are obtained. The peak potentials may also shift as the film becomes thicker, which may be attributed to factors such as heterogeneous electron-transfer kinetics or a decrease in electrical conductivity of electrolyte, in counter-ion mobility or conjugation length [14]. The current peaks were poorly defined and there was no obvious film on the electrode when aniline concentration was 0.1 M, meaning that this aniline concentration is the lowest limit; also, we consider that the polymer film could be significantly degraded in this diluted synthesis solution because the rate of degradation was probably higher than the rate of polymer growth [15].

We may compare these results in choline chloride based ionic liquids with other preliminary results of aniline electropolymerization obtained by us using aqueous acid media, although the reference electrode (Ag/AgCl instead of Ag) was changed. Fig. 4 illustrates this comparison. In Fig. 4a the oxidation peak potential of aniline in ChCl:urea 1:1 is about 1 V (*vs*. Ag reference) compared to the oxidation of aniline in acidic aqueous solution (Fig. 4c) where the anodic peak potential is around 0.35 V (*vs*. Ag, AgCl).

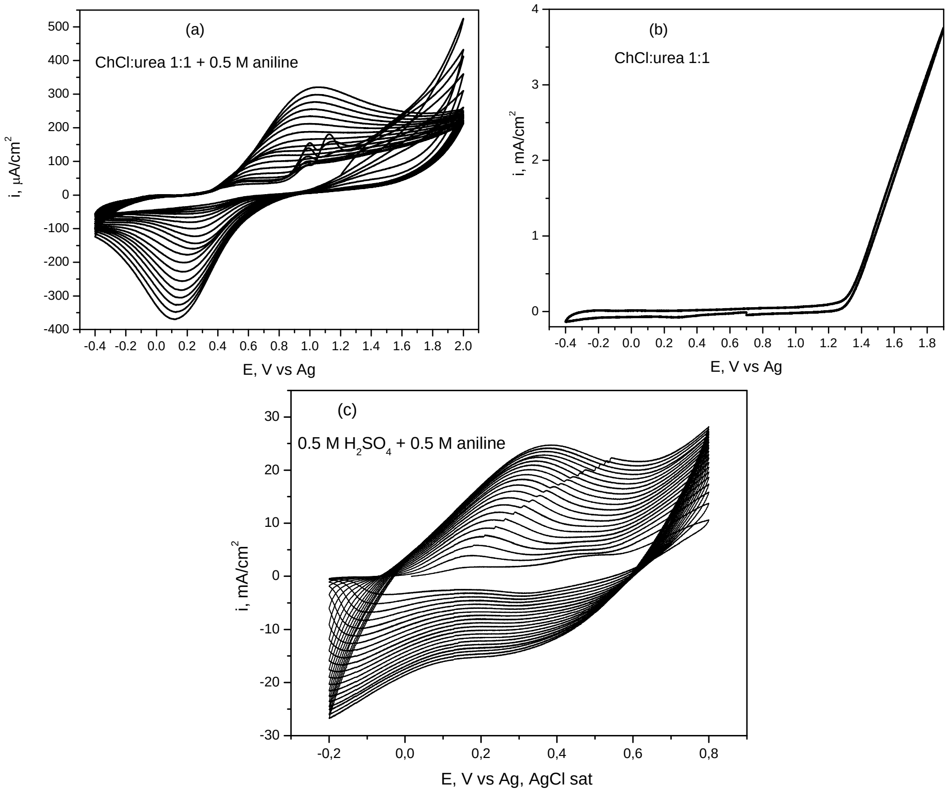

Fig. 4. Comparative CV curves on Pt electrode showing the growth of polyaniline film from ChCl:urea 1:1 ionic liquid with aniline 0.5 M (a), the voltammogram in ionic liquid without aniline (b) and the growth of polyaniline film from 0.5 M H_2SO_4 + 0.5 M aniline aqueous solution (c). Scan rate 50 mV/s, 25^0C

Fig. 4b shows clearly the absence of any electrode process in a blank ionic liquid if the potential sweep is up to 1.3 V anodic limit. Most important, the current density values for aniline oxidation in ionic liquids are lower with one order of magnitude than those in aqueous medium.

The increase of current densities in both media with the increase of the cycle number is certainly due to thickening of the polymeric film. Also, in all voltammograms the oxidation potential of monomer in ionic liquids is shifted gradually with the thickening of the polymer film, the process being self-catalyzed similarly with aniline polymerization in aqueous solutions.

However, we noticed that the cyclic voltammograms corresponding to the PANI growth on Pt from ionic liquids do not present the same shape as in aqueous solutions: it cannot be observed the peak related to the oxidation and formation of the polaron, the peak related to PANI degradation and the peak corresponding to the second oxidation process of the polymer. Therefore, the aniline polymerization mechanism in choline chloride:urea ionic liquids is different than in aqueous media.

3.2. Electrochemical behaviour of polyaniline

The electrochemical behaviour of polyaniline in electrolytes without aniline content was studied by cyclic voltammetry and electrochemical impedance spectroscopy.

Cyclic voltammetry. Fig. 5a illustrates a single pair of oxidation-reduction peaks of the polyaniline modified electrode in ionic liquid, unlike the polymer obtained in aqueous solution and tested in H_2SO_4 0.5 M solution, Fig. 5b, where three pairs of oxidation-reduction peaks appear.

The pair of redox peaks observed in Fig. 5a at 1 V (anodic) and 0.1 V (cathodic), respectively, may be assigned to the de-doping and doping of the polymer. Thus, the increased electric charge for anodic process of polymer is an indication of enhanced electrochemical activity of polyaniline film modified electrode during its doping.

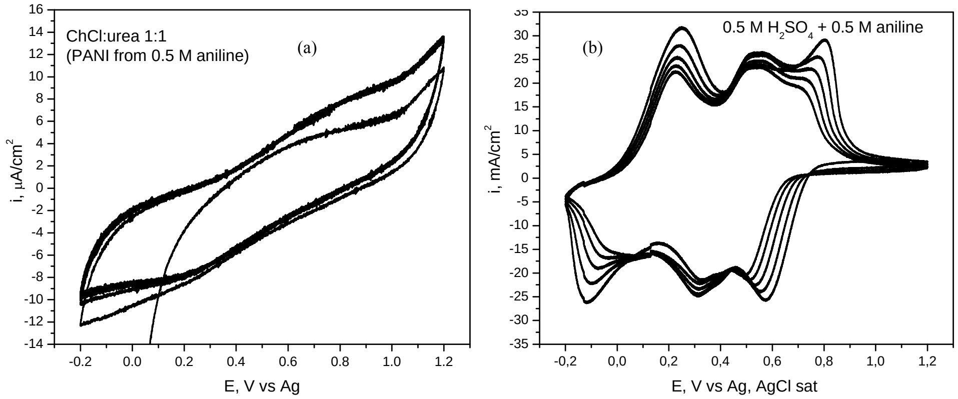

Fig. 5 Cyclic voltammograms of PANI modified platinum electrode in ChCl:urea 1:1 ionic liquid (PANI film obtained in 0.5 M aniline containing ChCl:urea 1:1) (a) and in H_2SO_4 0.5 M aqueous solution (PANI film was obtained in 0.5 M aniline containing H_2SO_4 0.5 M).
Scan rate 50 mV/s, 25^0C

On contrary, the first anodic peak is associated with the oxidation of the leucoemeraldine to emeraldine, the second peak is attributed to the presence of ortho-coupled polymers or to the oxidative degradation of polyaniline and the third peak is a further oxidation of the polyaniline to the form of quinoid diradical dication or to the further oxidation of polyaniline from emeraldine to pernigraniline.

The difference between the curves in Figs. 5a and 5b in the transfer solutions is caused by the characteristics of the obtained polymer, meaning that the polyaniline obtained from ionic liquid electrolyte has not the same activity as the polymer obtained from sulphuric acid solution. Regarding the positive and negative currents that are corresponding to the oxidation and reduction processes in ionic liquids, there is a small number of redox peaks in the cyclic voltammograms curves (not presented) which are attributed to the redox transition between the leucoemeraldine form and the emeraldine form of the PANI polymer. In the 1:1 ionic liquid as transfer solution, the highest current density on both branches (anodic and cathodic) was found for PANI synthesized from 0.1 M aniline solution. For PANI prepared from solutions with higher aniline concentration the current density decreased, a fact which can be attributed to the smooth polymer surface or to limiting of electrical conductivity of PANI layer.

Electrochemical impedance spectroscopy. The dependences between real Z_{Re} and imaginary Z_{Im} impedance components of PANI for a frequency range (10^5–0.01 Hz) are displayed in Figs. 6. The impedance plot as Nyquist spectrum is composed of a semicircle at high frequencies and a straight line with 45^0 slope at middle and low a.c. frequencies. Figs. 6a and 6c show clearly this shape.

The quite depressed semicircle recorded at high frequency region is considered to be due to the double layer charging process at the interface between a porous electrode surface and the electrolyte [16]. The linear part with the slope of near 45^0 appearing next to the semicircle indicates the diffusion limitation in the doping/undoping process [16].

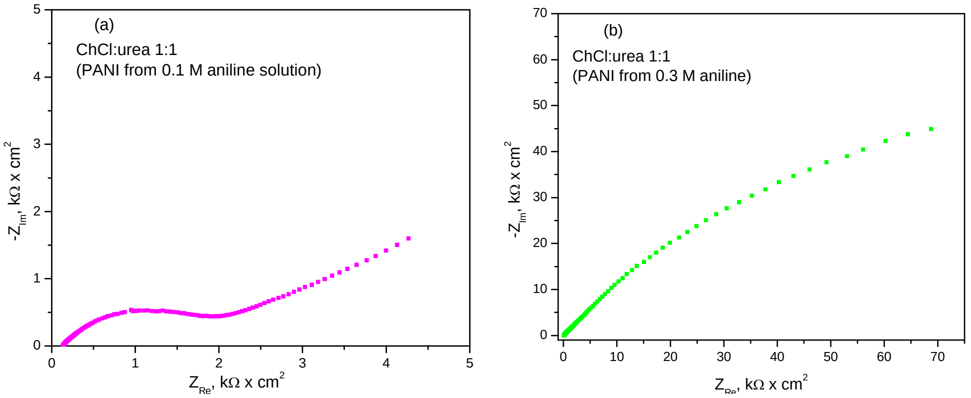

Fig. 6.1. Electrochemical impedance spectra of PANI film in ChCl:urea 1:1 transfer solution for the open-circuit potential of Pt electrode; the polymer film was prepared using the same ionic liquid containing: (a) 0.1 M, (b) 0.3 M

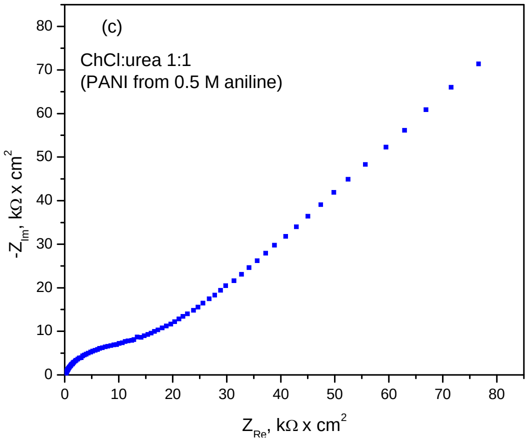

Fig. 6.2. Electrochemical impedance spectra of PANI film in ChCl:urea 1:1 transfer solution for the open-circuit potential of Pt electrode; the polymer film was prepared using the same ionic liquid containing: (c) 0.5 M aniline

The properties of polymeric film can be evaluated from the Nyquist diagrams. It clearly noticed that in the case of thicker films the electrical resistance values are lower than the ones for thinner films. For the cases where the polymer is not active the capacitive semicircle at high frequencies has the highest diameter as we obtained for the PANI film synthesized from 0.5 M aniline containing ionic liquid. The results are interpreted taking into account that the semicircle diameter correspond to the charge transfer resistance R_{ct}, a parameter which is inverse proportional to the faradaic current; large semicircles mean low current densities at a given polarization. Although the Fig. 6b shows not a clear semicircle, we may appreciate that the semicircle diameters have gradual increased values in a series of 2; 10 and 17 kΩcm^2 for PANI polymer prepared in solutions with 0.1, 0.3 and 0.5 M aniline concentrations, respectively. These results prove that the best electrochemical activity of polymeric film is for ionic liquid with 0.1 M aniline content.

4. Conclusions

In this work the polymerization of aniline on Pt electrode was carried out successfully in choline chloride-urea ionic liquids, with better results for 1:1 molar ratio of component than for 1:2 molar ratio. These room temperature ionic liquids are recognized as more friendly to the environment that conventional solvents. The experiments highlighted the occurrence of polymerization nuclei, the formation and growth of polyaniline films on platinum electrode, using as synthesis electrolyte the mixture of choline chloride:urea containing different concentrations of aniline. The mechanism the polymerization process is studied from the consecutive cyclic voltammograms (20 cycles).The oxidation potential of aniline is significantly affected by the composition of the ionic liquid and it is shifted upon polymer deposition onto working electrode in a direction that depends on the composition of ionic liquid used.

By comparing with PANI synthesis in aqueous H_2SO_4 solution, we noticed that using ionic liquids as polymerization media the polymer structure is changed.

The effect of aniline concentration on the electrochemical performances of PANI film obtained from ionic liquids was investigated, showing better electrochemical activity for films synthesized with dilute solution regarding aniline content. The electrochemical characterization of polyaniline film by cyclic voltammetry and electrochemical impedance spectroscopy has verified the involvement of the electrochemical activity of the polymer film (reversible process) in the region of anodic potentials. The studies have shown that PANI film obtained from choline chloride-urea based ionic liquids has electrochemical activity. However, the kinetic limitation of doping/dedoping process in transfer solution is most likely related to the ability of the anions to permeate the film, which is significantly different in ionic liquid compared to aqueous systems.

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