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THE INFLUENCE OF CURRENT DENSITY ON CHARGE/DISCHARGE CHARACTERISTICS OF POLYANILINE ELECTRODE

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ABSTRACT

Polyaniline (PANI) was electrochemically synthesized on graphite electrode galvanostaticaly from aqueous solution of 0.25 mol dm^{-3} aniline and 0.5 mol dm^{-3} p-toluenesulfonic acid. Charge capacity available for the exchange and the total theoretical weight of polyaniline polymerized on graphite electrode was determined. Characterization polianiline electrode was performed by cyclic voltametry in 0.5 mol dm^{-3} HCl. Based on the PANI electrodes behavior during the cyclization, was tested the possibility of practical application of polyaniline doped p-toluenesulfonic acid as the anode material of secondary electrochemical power sources.

INTRODUCTION

Conducting polymers (CP) is very interesting group of polymers due to their specific characteristic including electrical conductivity, mechanical strength, corrosion resistance and the possibility of their chemical and electrochemical synthesis. Therefore, the study of the synthesis, structure and properties of these materials in the world pays specail attention to the las twenty years. CP have found application in microelectronics, optoelectronics, the active protection of metals and alloys from corrosion and, lately as electrode materials for application in electrochemical energy sources [1].

Although the CP can be synthesized an the chemical and electrochemical oxidative polymerization, electrochemical synthesis is better because its performance is not the oxidizing agent is used directly in its conductive form [2]. CP can be electrochemically sythesized by different techniques: cyclic voltametry, potentioststic and galvanostatic technique. The most applicable is galvanostatic tehnique that allows control of polymerization in terms of thickness and morphology of the deposit.

The best known systems that are used in electrochemical energy sources usind electollytes based on aqueous solutions of the systems are composed of polymers based in polianiline (PANI) in combinatiob with electronegative metals (usually zinc) [3-10]. PANI is very interesting because of its unique charge transfer, an interesting behavior in aqueous solutions and features that no adverse impact on the environment. Although it appears that these systems can meet most of the 3-E criteria (Energetic, Economic and Enviromental): energy (high specific and volumetric capacity), economic (low cost of developing and maintaining a large number od cycles), the criteria of Environmental protection (intoxic, energy efficiency, ease of recycling) are the main factors of efficiency of electrochemical power sources [11-12], these systems have found practical application. The main reason is the appearance of degradation of polyaniline [13, 14].

The aim of this paper is to investigate the influence of the current density on charge/discharge characteristic of polianiline electrode.

EXPERIMENTAL

Polyaniline on graphite electrode was formed by anodic polymerization from aqueous solution of 0,5 mol dm^{-3} p- toluensulfonic acid and 0.25 mol dm^{-3} aniline at constant current density of 2.0 mA cm^{-2}. Prior to use aniline (p.a. Aldrich) was distilled in argon. The working electrode was first mechanically polished with fine emery papers (2/0, 3/0 and 4/0) and than with polishing alumina (1μm Banner Scientific Ltd.) on polishing cloths (Buehler Ltd.). The traces of the polishing alumina were removed from the electrode surface ultrasonically during 10 min. After polymerization, PANI electrode was dedoped with current density of 1.0 mA cm^{-2}, washed with bidistilled water and than investigated in 0.5 mol dm^{-3} HCl. The characterization of *p* – TS doped polyaniline was firstly characterized by cyclic voltammetry using different scan rates. The efficiency of charge/discharge process was investigated using different discharge current densities in the range of 0.25 – 2.0 mA cm^{-2}. The experiments were carried out in three compartment electrochemical cells. Saturated electrode served as reference, while platinum foil was used as counter electrode. All electrochemical experiments were performed using GMRY PC3 potentiostat/galvanostat controlled by PC.

RESULTS AND DISCUSSION

Aniline electropolymerization on graphite electrode from 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline at constant current density of 2.0 mA cm^{-2} during 1080. Electrochemical polymerization of aniline occurs together with insertion of *p*-toluen sulfonic anion (doping) according to:

$$(PANI)_n + nyp\text{-}TS^- \rightarrow [PANI^{y+}(p\text{-}TS^-)]_n + nye^- \qquad (1)$$

After synthesis, electrode was discharged (dedoped) in the same solution. From the ratio of the charge delivered during discharge and the charge used for the synthesis it could be concluded that 30% of the overall mass is available for the current exchange.

Fig. 1. shows cyclic voltammograms of polyaniline electrode obtained using different scan rates in the potential range between -0.6 and 0.6 V vs. SCE.

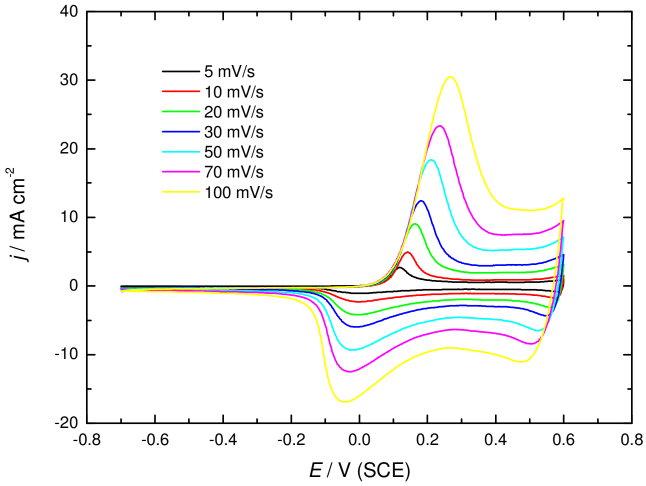

Fig. 1. Cyclic voltammograms of polyaniline electrode in 0.5 mol dm^{-3} HCl obtained by different scan rates (as marked in Fig.) in the potential range – 0.7 – 0.6 V.

From the data displayed at Fig. 1, dependences of peak current on squere rt. of scan rate is given on Fig. 2.

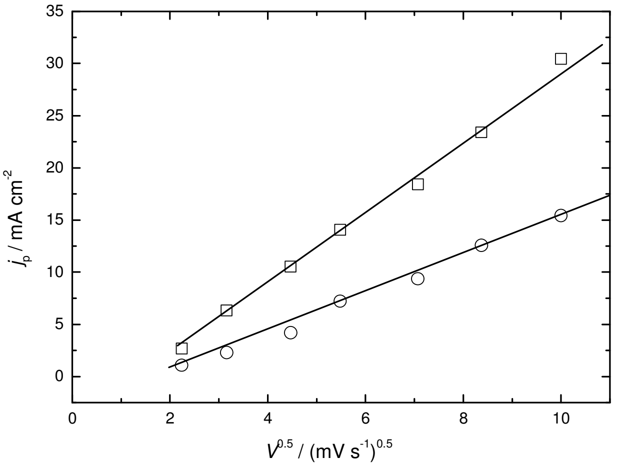

Fig. 2. Dependences of peak currents on square rt. of scan rate.

Linear dependences of current peak on sq. rt. of scan rate is linear indicating diffusion control of ions doping/dedoping process.

Polyaniline was subjected to charge / discharge by different current densities in the range of 0.25 to 2.0 mA cm^{-2}, charging process was performed until potential of 0.5 V was reached, while discharge was performed to potential of -0.4 V, and data are given in Table 1. and in Fig. 3.

Table 1. Charge and discharge time and capacities obtained by different current densities.

j = 0,25 mA cm^{-2}		
	Charge	discharge
t / s	1540	1520
Q / C cm^{-2}	0,385	0,380
j =0,5 mA cm^{-2}		
	charge	discharge
t / s	810	790
Q / C cm^{-2}	0,405	0,395
j =0,75 mA cm^{-2}		
	charge	discharge
t / s	590	550
Q / C cm^{-2}	0,442	0,412

j =1,0 mA cm^{-2}		
	Charge	discharge
t / s	370	350
Q / C cm^{-2}	0,370	0,350
j =1,5 mA cm^{-2}		
	charge	discharge
t / s	280	250
Q / C cm^{-2}	0,420	0,375
j =2,0 mA cm^{-2}		
	charge	discharge
t / s	190	170
Q / C cm^{-2}	0,380	0,340

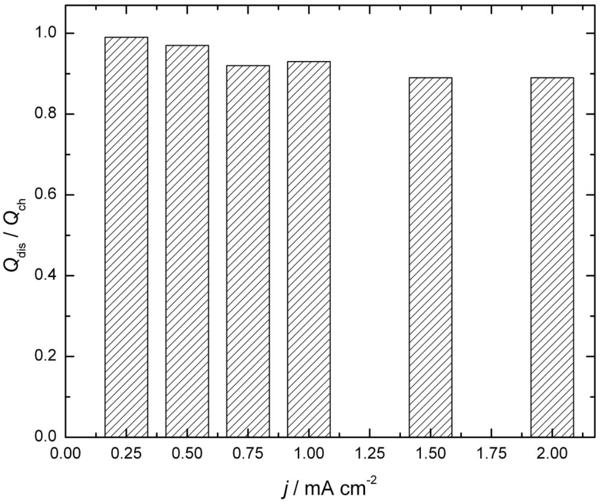

Fig 3. Calculated discharge/charge capacities ratio of polyaniline electrode in 0.5 mol dm^{-3} HCl, obtained by different current densities in the range of 0.5 – 2.00 mA cm^{-2}.

As it could bee seen from both Table1 and Fig. 3. Maximum efficiency of charge/discharge process expreced as ratio of discharge and charge capacities was achieved at low current densities of 0.25 (practically all the charge is delivered during discharge process, Q_{dis} / Q_{ch} ~ 100 %) after which the discharge/ charge ratio is lowered but remained constant with current densities in the range of 0.50 – 2.0 mA cm^{-2}. This investigation is still in progress but obtained results suggested that polyaniline doped by *p*-toluen sulfonic acid could be considered as interesting material for rechargeable power sources.

CONCLUSION

Polyaniline electrode was successfully obtained by galvanostatic deposition of polyaniline from aqueou *p*- toluen sulfonic acid electrolite containing aniline. Polyaniline electrode was investigated in by cyclic voltammetry galvanostatic charge/discharge. It was observed that polyaniline doped by *p*-toluen sulfonic anion could be considered as anodic material for electrochemical rechargeable power sources.

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