

# The influence of current density on charge/discharge characteristics of polyaniline electrode

Gvozdenovic, M.<sup>a</sup>, Jugovic, B.<sup>b</sup>, Jambrec, D.<sup>c</sup>, Grgur, B.<sup>a</sup>, Trisovic, T.<sup>b</sup>, Stevanovic, J.<sup>d</sup>

<sup>a</sup> Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

<sup>b</sup> Institute of Technical Science, Serbian Academy of Science and Arts, Knez Mihajlova 35, 11000 Belgrade, Serbia

<sup>c</sup> Inovation center- Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

<sup>d</sup> IHTM-Institute of electrochemistry, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia

## 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 special attention to the last 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 by 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 synthesized by different techniques: cyclic voltammetry, potentiostatic and galvanostatic technique. The most applicable is galvanostatic technique 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 using electrolytes based on aqueous solutions of the systems are composed of polymers based on polyaniline (PANI) in combination 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 Environmental): energy (high specific and volumetric capacity), economic (low cost of developing and maintaining a large number of cycles), the criteria of Environmental protection (nontoxic, 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 polyaniline electrode.

## EKSPERIMENTAL

Polyaniline on graphite electrode was formed by anodic polymerization from aqueous solution of 0,5 mol dm<sup>-3</sup> p-toluensulfonic acid and 0.25 mol dm<sup>-3</sup> aniline at constant current density of 2.0 mA cm<sup>-2</sup>. 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 then with polishing alumina (1 μm 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<sup>-2</sup>, washed with bidistilled water and then investigated in 0.5 mol dm<sup>-3</sup> 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<sup>-2</sup>. 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

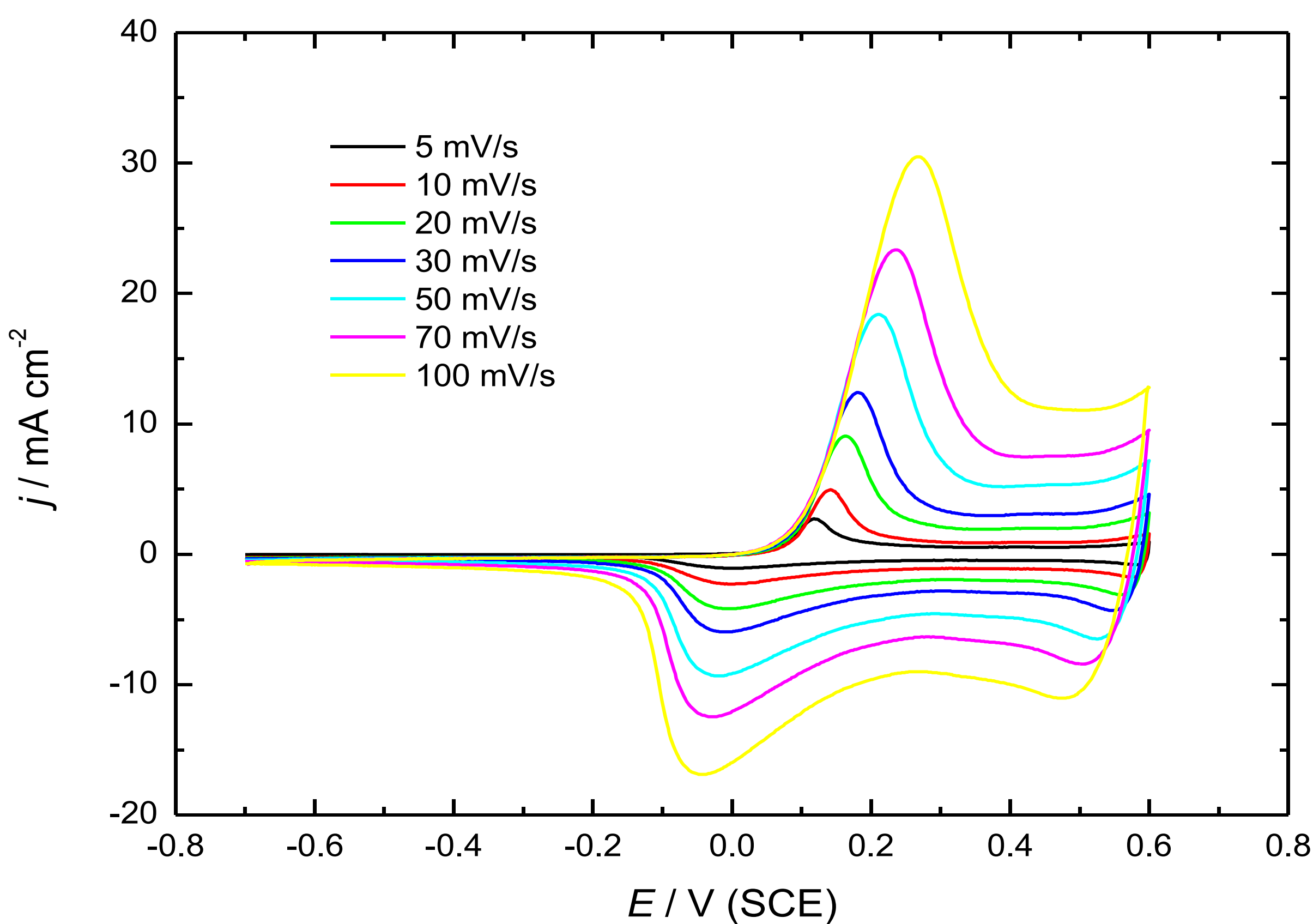


Fig. 1. Cyclic voltammograms of polyaniline electrode in 0.5 mol dm<sup>-3</sup> HCl obtained by different scan rates (as marked in Fig.) in the potential range -0.7 – 0.6 V.

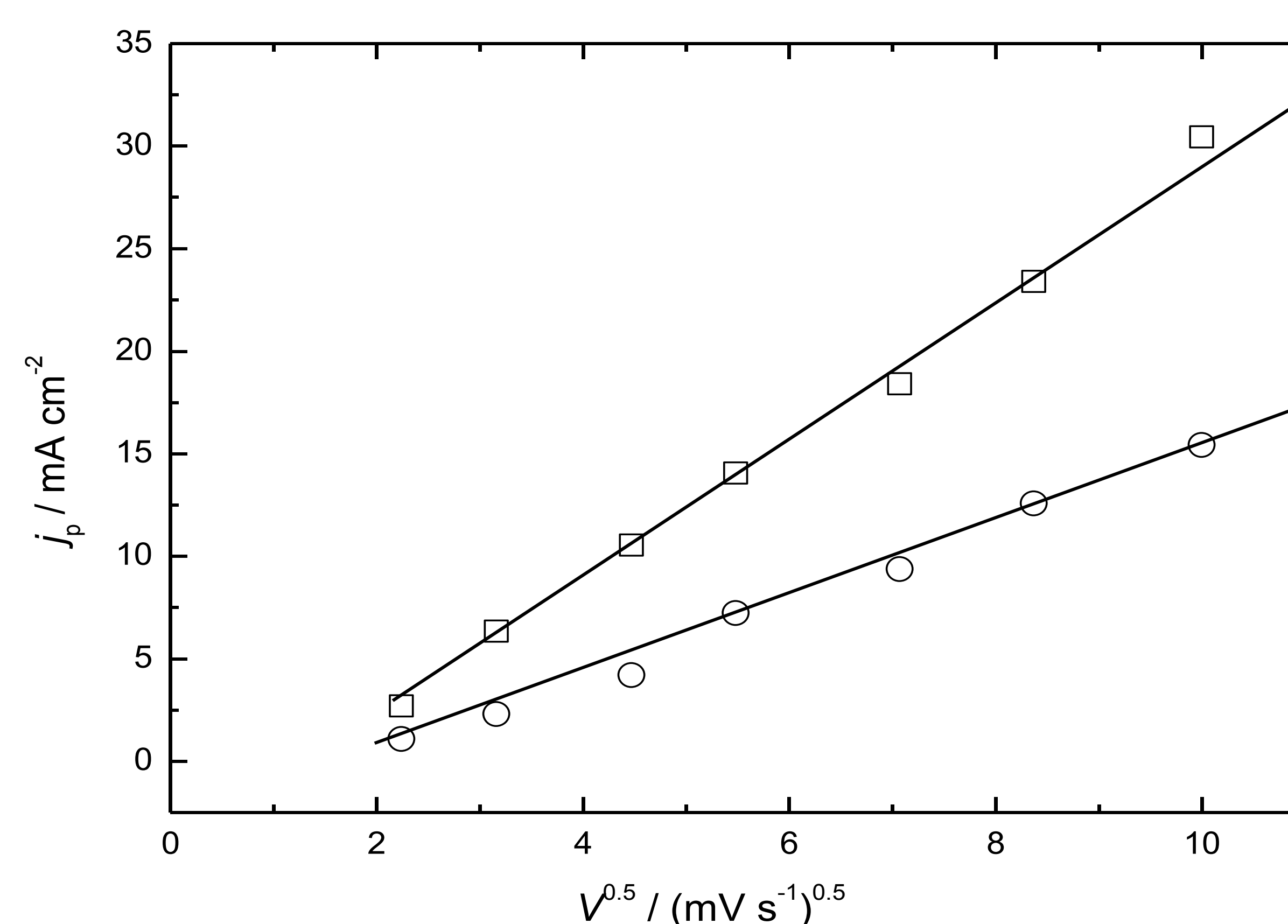


Fig. 2. Dependences of peak currents on square root of scan rate.

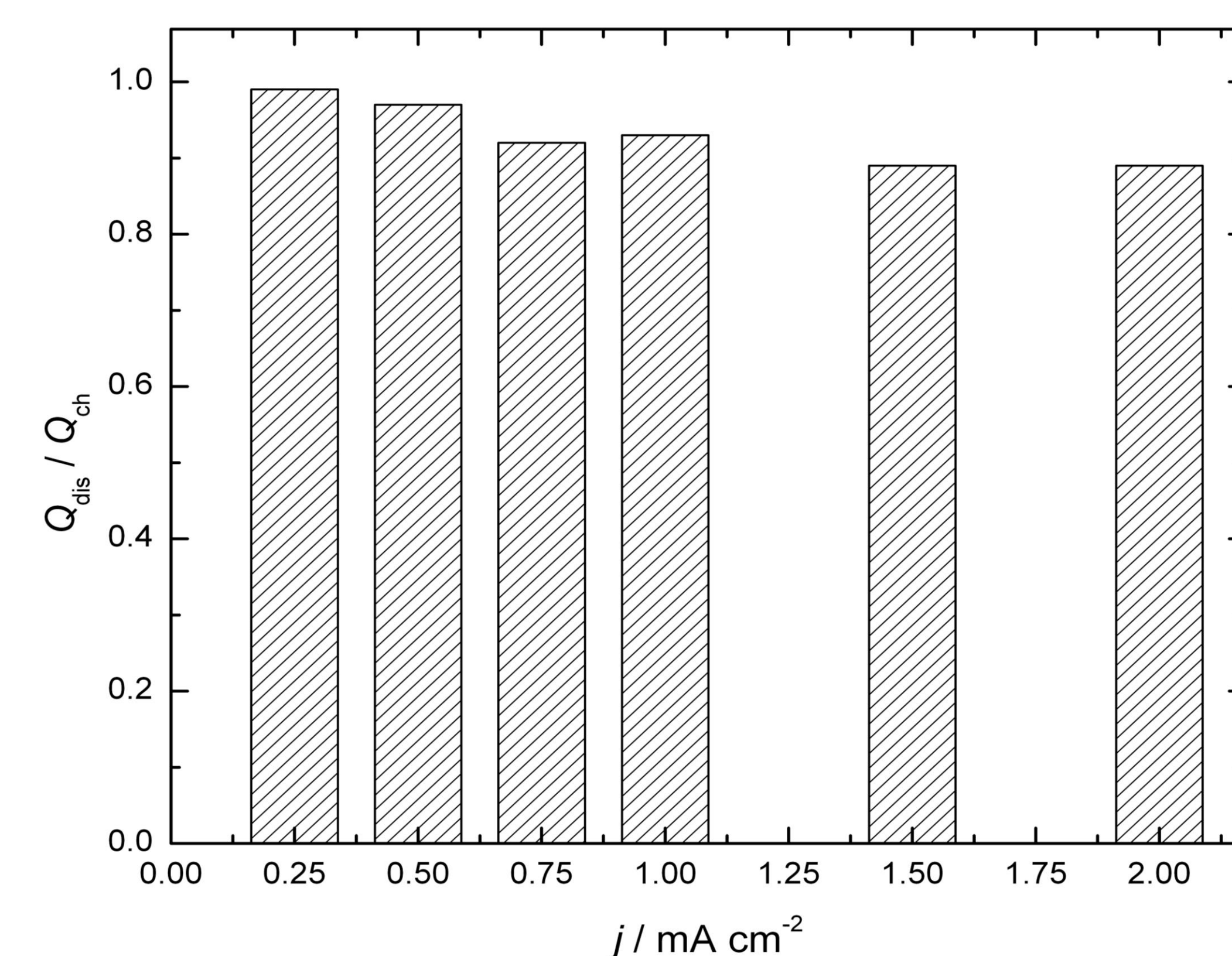


Fig 3. Calculated discharge/charge capacities ratio of polyaniline electrode in 0.5 mol dm<sup>-3</sup> HCl, obtained by different current densities in the range of 0.5 – 2.00 mA cm<sup>-2</sup>.

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

$j = 0,25 \text{ mA cm}^{-2}$			$j = 1,0 \text{ mA cm}^{-2}$		
	Charge	discharge		Charge	discharge
$t / s$	1540	1520	$t / s$	370	350
$Q / C \text{ cm}^{-2}$	0,385	0,380	$Q / C \text{ cm}^{-2}$	0,370	0,350
$j = 0,5 \text{ mA cm}^{-2}$			$j = 1,5 \text{ mA cm}^{-2}$		
	charge	discharge		charge	discharge
$t / s$	810	790	$t / s$	280	250
$Q / C \text{ cm}^{-2}$	0,405	0,395	$Q / C \text{ cm}^{-2}$	0,420	0,375
$j = 0,75 \text{ mA cm}^{-2}$			$j = 2,0 \text{ mA cm}^{-2}$		
	charge	discharge		charge	discharge
$t / s$	590	550	$t / s$	190	170
$Q / C \text{ cm}^{-2}$	0,442	0,412	$Q / C \text{ cm}^{-2}$	0,380	0,340

From the data displayed at Fig. 1, dependences of peak current on square root of scan rate is given on Fig. 2. Linear dependences of current peak on square root 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<sup>-2</sup>, 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. As it could be seen from both Table 1 and Fig. 3. Maximum efficiency of charge/discharge process expressed 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,  $Q_{\text{dis}} / Q_{\text{ch}} \sim 100\%$ ) after which the discharge/charge ratio is lowered but remained constant with current densities in the range of 0.50 – 2.0 mA cm<sup>-2</sup>. 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.

## REFERENCES

- [1] Malinauskas A, Malinauskienė J, Ramanavičius A. *Conducting polymer-based nanostructured materials: electrochemical aspects*. Nanotechnology 2005;16:R51-R62.
- [2] Skotheim TA, editor. *Handbook of Conducting Polymers*. New York: Marcel Dekker; 1986.
- [3] Sima M, Visan T, Buda M. *A comparative study of zinc-polyaniline electrochemical cells having sulfate and chloride electrolytes*. Journal of Power Sources 1995;56:133-136.
- [4] Kan J, Xue H, Mu S. *Effect of inhibitors on Zn-dendrite formation for zinc-polyaniline secondary battery*. Journal of Power Sources 1998;74:113-116.
- [5] Rahmanifar M S, Mousavi M F, Shamsipur M, Ghaemian M. *What is the limiting factor of the cycle-life of Zn-polyaniline rechargeable batteries*. Journal of Power Sources 2004;132:296-301.
- [6] Karami H, Mousavi M F, Shamsipur M. *A new design for dry polyaniline rechargeable batteries*. Journal of Power Sources 2003;117:255-259.
- [7] Jugović B Z, Trišović T Lj, Stevanović J, Maksimović M, Grgur B N. *Novel electrolyte for zinc-polyaniline batteries*. Journal of Power Sources 2006;160:1447-1450.
- [8] Jugović B Z, Trišović T Lj, Stevanović J, Maksimović M, Grgur B N. *Comparative studies of chloride and chloride/citrate based electrolytes for zinc-polyaniline batteries*. Electrochimica Acta 2006;51:6268-6274.
- [9] Rahmanifar M S, Mousavi M F, Shamsipur M, Heli H. *A study on open circuit voltage reduction as a main drawback of Zn-polyaniline rechargeable batteries*. Synthetic Metals 2005;155:480-484.
- [10] Mirmohseni A, Solhjo R. *Preparation and characterization of aqueous polyaniline battery using a modified polyaniline electrode*. European Polymer Journal 2003;39:219-223.
- [11] Rüetschi P. *Energy storage and the environment: the role of battery technology*. J. Power Sources. 1993;42:1-7.
- [12] Beck F, Rüetschi P. *Rechargeable batteries with aqueous electrolytes*. Electrochimica Acta. 2000;45:2467-2482.
- [13] Arsov Lj D, Plieth W, Kofmehl G. *Electrochemical and Raman spectroscopic study of polyaniline; influence of the potential on the degradation of polyaniline*. J. Sol. St. Electro. 1998;2:355-361.