**Slovak Society of Chemical Engineering**

**Institute of Chemical and Environmental Engineering**

**Slovak University of Technology in Bratislava**

# PROCEEDINGS

**38th International Conference of Slovak Society of Chemical Engineering**

**Hotel Hutník**

**Tatranské Matliare, Slovakia**

**May 23 – 27, 2011**

**Editor: J. Markoš**

Jugovic, B., Gvozdenovic, M., Trisovic, T., Stevanovic, J., Grgur, B.: Electrochemical behavior of polyaniline in chloride/citrate electrolyte, Editor: Markoš, J., In *Proceedings of the 38th International Conference of Slovak Society of Chemical Engineering*, Tatranské Matliare, Slovakia, 963–967, 2011.

# Electrochemical behavior of polyaniline in chloride/citrate electrolyte

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## Abstract

Polyaniline electrode, was obtained by electrochemical polymerization at constant current density of 2.0 mA cm$^{-2}$ from aqueous solution of 1.0 mol dm$^{-3}$ HCl containing 0.25 mol dm$^{-3}$ aniline. Electrochemical characterization of the polyaniline electrode in chloride and chloride/citrate electrolyte, for different anodic potential limits, was performed using cyclic voltammetry and galvanostatic measurements. It was observed that for anodic potential 0.32 V, higher electrode capacity in chloride/citrate was obtained. For anodic potential limit of 0.50 V, faster decrease of the electrode capacity in chloride/citrate electrolyte was also observed. It was suggested that influence of both chloride and citrate anions has to be taken into account.

Key words: polymers, electrochemical techniques, electrochemical properties

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## 1. Introduction

Due to their unique properties, such as: mechanical strength, electrical conductivity, corrosion stability, possibility of chemical and electrochemical synthesis, electroconducting polymers (ECP) were considered in wide area of practical application such as: microelectronics, optoelectronics, corrosion protection, sensors, electromagnetic shielding, and electrochemical power sources [1-8]

ECP could be synthesized by both chemical and electrochemical oxidative polymerization. However, electrochemical synthesis is favorable permitting the control of the reaction and polymerization without oxidizing agent together with doping by organic or inorganic ions in a single step.

Among large number of ECP, polyaniline (PANI) is the most investigated as cathode material in aqueous based electrochemical power sources [5-13]. Although systems consisted of PANI cathode combined to electronegative metal (mainly zinc) anode, are likely to accomplish most of the three E criteria: Energy (high energy content with respect to volume and weight), Economics (low manufacturing and maintenance costs, long service life), Environment (toxic free, safety, low energy consumption, easy to recycle) elaborated as the determining factors of an electrochemical power system success [14,15] they still have not been commercialized from several reasons.

## 2. Experimental

Electrochemical synthesis of PANI on graphite electrode ($S = 0.64$ cm$^2$) was performed at constant current density of 2 mA cm$^{-2}$ from aqueous solution of 1.0 mol dm$^{-3}$ HCl (p.a. Merck) and 0.25 mol dm$^{-3}$ aniline. After polymerization, PANI electrode was discharged in the same solution with 1 mA cm$^{-2}$ to the potential of – 0.6 V, than rinsed in bidestilled water, and transferred into electrochemical cell containing for further characterization. Prior to use aniline (p.a. Aldrich) was distilled in argon atmosphere. The working electrode, cylindrically shaped graphite inserted in Teflon holder was first mechanically polished with fine emery papers (2/0, 3/0 and 4/0,

respectively), 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 in an ultrasonic bath during 5 min.

PANI electrode was characterized using cyclic voltammetry and galvanostatic cyclization measurements in chloride (0.5 mol dm$^{-3}$ NH$_4$Cl and 0.2 mol dm$^{-3}$ ZnCl$_2$) and chloride/citrate (0.5 mol dm$^{-3}$ NH$_4$Cl and 0.2 mol dm$^{-3}$ ZnCl$_2$ with addition of 0.3 mol dm$^{-3}$ Na-citrate). All experiments were performed in standard three compartment electrochemical cell at ambient temperature (22 $^0$C). Saturated calomel electrode was used as reference, while Pt wire served as counter electrode. The measurements were carried out using PAR 273A potentiostat/galvanostat interfaced to PC.

## 3. Results and discussion

Electrochemical polymerization of aniline on graphite electrode from 1.0 mol dm$^{-3}$ and 0.25 mol dm$^{-3}$ aniline at constant current density of 2.0 mA cm$^{-2}$ during 1080 s is given in insert of Fig.1. After polymerization, PANI electrode was discharged with current density of 1 mA cm$^{-2}$, and transferred to another electrochemical cell for further investigation. Six successive cyclic voltammograms ($v$ = 20 mV s$^{-1}$) of PANI electrode are shown in Fig.1. Voltamogramms are characterized by constant charge increase as a result of formation of insoluble PANI, while anodic and cathodic correspond to different oxidation forms of PANI.

As seen in insert Fig.1, PANI polymerization occurred at potentials around 0.7 V, meaning that polymerization undergoes through formation of perningraniline salt. Comparing the polymerization charge of 0.60 mAh cm$^{-2}$ and discharge charge of ~ 0.14 mAh cm$^{-2}$, it could be concluded that only 23 % of the total mass was available for charge exchange, while rest of the charge refers to formation of inactive PANI oligomers and degradation products.
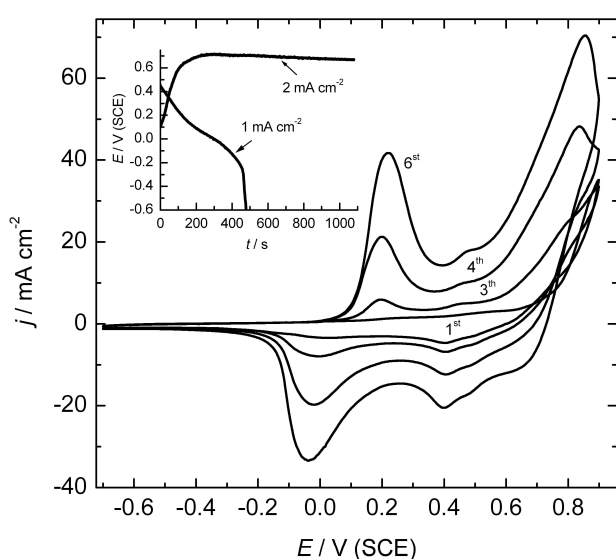


Fig. 1. Galvanostatic curve of electrochemical polymerization of aniline at graphite electrode in 1.0 mol dm$^{-3}$ HCl and 0.25 mol dm$^{-3}$ aniline, $j$ = 2.0 mA cm$^{-2}$. Insert: Cyclic voltammogram of PANI electrode in 1.0 mol dm$^{-3}$ HCl and 0.25 mol dm$^{-3}$ aniline ($v$ = 20 mV s$^{-1}$).
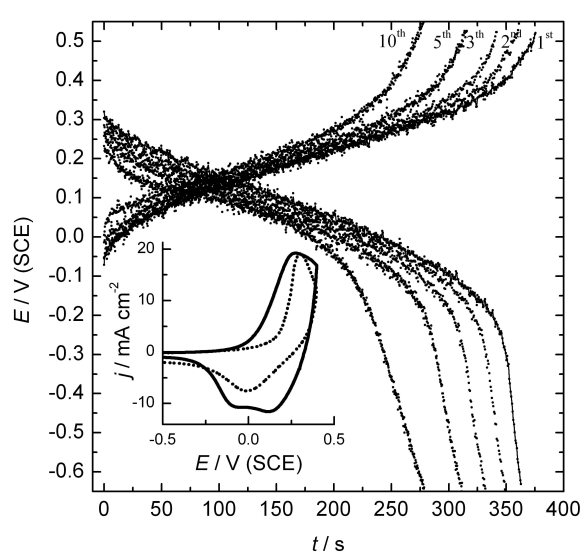
Fig.2. Charge/discharge curves of PANI electrode during ten cycles, $j$ = 1 mA cm$^{-2}$ in chloride/citrate electrolyte for anodic potential limit of 0.50 V. Insert: cyclic voltammograms:(—)-before and (…)-after ten cycles, $v$ = 20 mV s$^{-1}$.

It was previously showed [10] that anodic potential limit had exhibited influence on charge/discharge characteristics of the PANI electrode, resulted in decrease of the electrode capacity during cyclization. Bearing in mind that addition of citrate anions had enhanced characteristics of negative zinc electrode [19], charge/discharge behavior of the PANI electrode were investigated in chloride/citrate electrolyte. In Fig. 2 and in Fig.3 charge/discharge curves of the PANI electrode in chloride/citrate electrode during ten cycles obtained by current density of 1

mA cm$^{-2}$ and differnt anodic potential limits of 0.5 V and 0.32 V are given respectively . Inserts of Fig.2 and Fig.3 show cyclic voltammograms before and after ten cycles of the PANI electrode in chloride/citrate electrolyte.

   As seen in Fig.2 and 3, anodic potential limit had grate influence on charge/discharge behaviour of the PANI electrode in chloride/citrate electrode. For anodic potential limit of 0.5 V (Fig.2) time for charging/discharging constantly decreased over time. As seen in insert of Fig.2, cyclic voltamograms taken before and after ten cycles showed capacity lost, suggesting that strong PANI degradation had occurred. For anodic potential limit of 0.32 V (Fig.3) charge/discharge curves of the PANI electrode in chloride/citrate electrolyte were the same over ten cycles, meaning that electrode capacity remained practically constant. This funding indicates that degradation of PANI had not occurred. As seen in insert of Fig.2, cyclic voltammograms of the PANI electrode before and after ten cycles remained the same, confirming again the fact that there was no PANI degradation during cyclization. It is interesting to mention that charge/discharge capacities of the PANI electrode were almost two times higher in chloride/citrate than in chloride electrolyte (given in dot lines on Fig.3).

   The dependences of calculated charge and discharge capacities of the PANI electrode from Fig. 2 and 3 on cycle number is given in Fig.4.
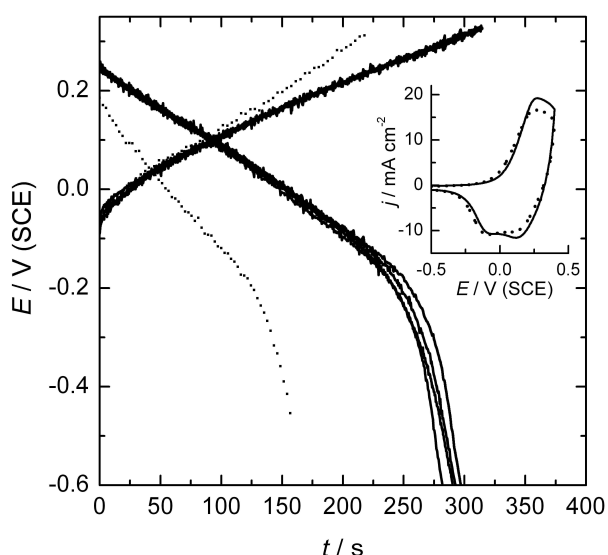


Fig.3. Charge/discharge curves of PANI electrode during ten cycles, $j = 1$ mA cm$^{-2}$ in chloride/citrate-ful lines and chloride electrolyte-dot lines, for anodic potential limit of 0.32 V., dot lines-chloride. Insert: cyclic voltammograms:(—)-before and (…)-after ten cycles, $v = 20$ mV s$^{-1}$.
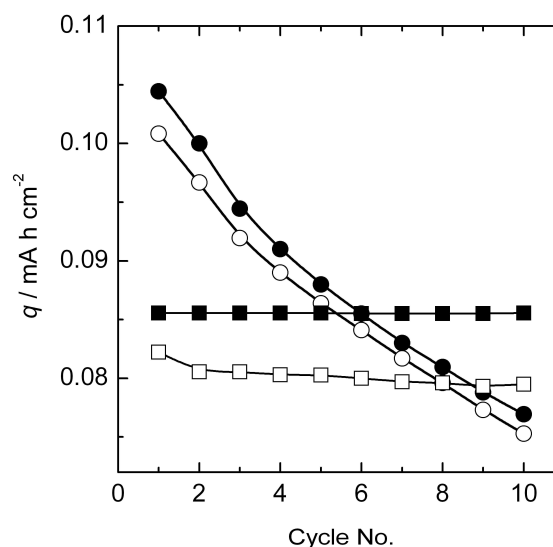
Fig.4. Dependences of PANI electrode capacities on cycle number in chloride/citrate electrolyte, for anodic potential limit of 0.5 V: (•)-charge, (○)-discharge and 0.32V (■)-charge, (□)-discharge. Insert: Columbic efficiency for anodic potential limit of:  (•)-0.5 V and (■)-0.32 V.

   As seen in Fig.5, for anodic potential limit of 0.50 V, permanent lost (around 25%) of capacity during ten cycles was observed even though the initial capacity was higher than for anodic potential of 0.50 V comparing to 0.32 V. On contrary, there was practically no capacity lost observed for the potential limit of 0.32 V. Since PANI was always polymerized under the same conditions, the decrease of the capacity for higher anodic potential limit of 0.5 V in chloride/citrate electrolyte could be connected to the presence of citrate anions. The effect of the doping anions, proposed by Yang et al. [16] could be attributed to the hydrophobic effect following the Hofmeister series [17]:

$$ClO_4^-. > NO_3^- > I^- > Br^- > Cl^- > F^- > HPO_4^{2-} > SO_4^{2-}. > citrate^{3-}$$
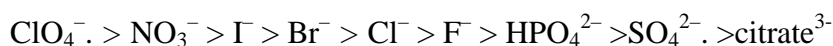
According to this, perchlorate ions are the most hydrophobic, citrate ions are the most hydrophilic, while chloride are in the middle. So, it was expected that chloride ions would form relatively stabile ion pars in oxidized PANI film, therefore PANI degradation could be limited to certain degree by dissociation of the ion par, resulting in slower degradation kinetics of PANI in chloride than in chloride citrate electrolyte.

In Fig.5 cyclic voltammograms of the PANI electrode in chloride, chloride/citrate and in pure citrate (0.3 mol dm$^{-3}$ Na-citrate) are given.

As it can be seen in Fig.5, doping of PANI by anions in all electrolytes started at the same potential of about -0.15 V. Peak potential of emeraldine salt in chloride and chloride/citrate electrolytes occurred at almost same potential of ~ 0.25 V, while the peak potential in pure citrate electrolyte was shifted for more than 100 mV in positive direction. In chloride/citrate electrolyte doping preceded through broad peak, indicating that both chloride and citrate anions were involved in doping. It could be suggested that at lower potentials doping by chloride occurred, while at more positive potentials doping by citrate anions might have occurred. Comparing the values of the potentials in doping area for chloride and chloride/citrate electrolytes for the same value of current densities, it seams that doping reaction in chloride/citrate was shifted for about 30 mV in negative direction. This negative shift of the potential resulted in higher charge/discharge capacities obtained in chloride/citrate than in chloride electrolyte. On the other hand, in order to avoid fast PANI degradation and decrease in charge exchange ability, it is highly recommender that anodic potential limit during cyclization should not exceed ~ 0.35 V.



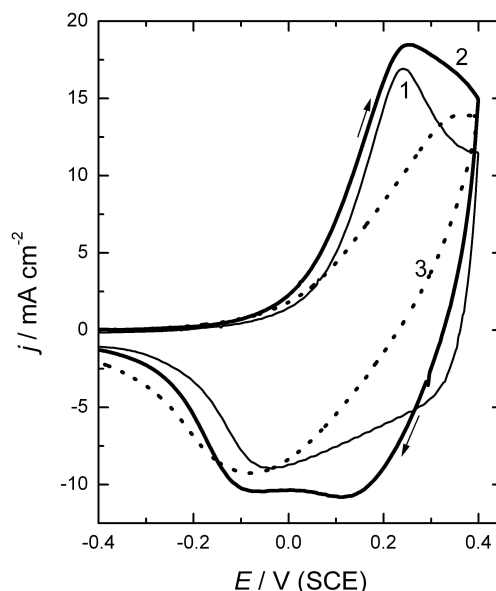Fig.5. Cyclic voltammograms of PANI electrode in: chloride, 2-chloride/citrate and 3-citrate electrolyte, $v$ = 20 mV s$^{-1}$.

## 4. Conclusion

Electrochemical synthesis of PANI on graphite from aqueous solution of hydrochloric acid containing aniline monomer was performed galvanostatically. The polymerization charge was 0.60 mAh cm$^{-2}$ while discharge charge was ~ 0.14 mAh cm$^{-2}$, so it was concluded that only 23 % of the total polymer mass was available for charge exchange, while rest of the charge refers to formation of inactive PANI oligomers and degradation products. Based on electrochemical studies, it was concluded that in chloride/citrate electrolyte both citrate and chloride anions played role in doping. The faster decrease in charge/discharge capacity in chloride/citrate electrolyte compared to chloride for potential limit of 0.50 V was explained by hydrophilic effect of citrate ions, while higher charge/discharge capacities were explained by negative doping potential shift of about 30 mV. It was recommended that charging potential should not exceed 0.35 V.

## Acknowledgment

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