

Characterization of electrochemically synthesized PANI on graphite electrode for potential use in electrochemical power sources

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ARTICLE INFO

Article history:

Received 22 August 2008

Received in revised form 6 October 2008

Accepted 27 October 2008

Keywords:

Electropolymerization

Polyaniline

Rechargeable power sources

ABSTRACT

Polyaniline (PANI) on graphite electrode was synthesized electrochemically under galvanostatic condition at current density of 2.0 mA cm^{-2} from aqueous solution of 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline monomer. Electrochemical characterization of the PANI electrode was performed in 0.5 mol dm^{-3} HCl using cyclic voltammetry and galvanostatic measurements. The overall charge capacity of the PANI electrode was estimated to be $0.154 \text{ mAh cm}^{-2}$, which corresponds to 25% of the theoretical mass of PANI available for doping exchange. It was observed that during initial cyclization at low pH, the extent of PANI degradation products was insignificant and practically had no influence on the charge/discharge characteristics of the PANI electrode.

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1. Introduction

Electroconducting polymers (ECP) have drawn much attention in last decades, due to their unique properties such: mechanical strength, electrical conductivity, corrosion stability, possibility of chemical and electrochemical synthesis. Such unique properties of ECP were considered in wide area of practical application like: microelectronics, optoelectronics, active corrosion protection, and electrochemical power sources [1].

ECP can be obtained using chemical and electrochemical oxidative synthesis. However, for the some applications electrochemical synthesis without oxidizing species is favorable, permitting the control of the reaction [2]. Electropolymerization can be achieved by different electrochemical techniques such as cyclic voltammetry, potentiostatic or galvanostatic technique. Galvanostatic technique is common for the practical applications, permitting control over some polymerization process parameters regarding the morphology and thickness of the deposit.

Among numerous ECP, polyaniline (PANI) as cathode combined to electronegative metals (mainly zinc) as anode, are the most extensively investigated systems for the application in aqueous based electrochemical power sources [3–11]. Although these systems are likely to accomplish most of the three E criteria: Energy (high energy content with respect to volume and weight), Eco-

nomics (low manufacturing and maintenance costs, long service life), Environment (toxic free, safety, low energy consumption, easy to recycle) elaborated by Rüetschi and Beck [12,13] as the determining factors of an electrochemical power system success, they still have not been commercialized. The main reason is connected to the degradation process of PANI at potentials more positive than 0.5 V . [14,15].

Electrochemical studies, at the first place cyclic voltammetry, were shown to be particularly useful in investigations of the basic aspects of the polymer growth and degradation mechanisms [16]. Therefore, the aim of this paper was to investigate the influence of the potential on degradation process of electrochemically synthesized PANI electrode in aqueous hydrochloric acid solution, using electrochemical techniques, as a possible electrode material for aqueous based rechargeable power sources.

2. Experimental

Electrochemical synthesis of PANI on graphite electrode ($S=0.64 \text{ cm}^2$) 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. 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 ($1 \mu\text{m}$, 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 0.5 mol dm^{-3} HCl. For all experiments the following procedure was used. 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 bidistilled

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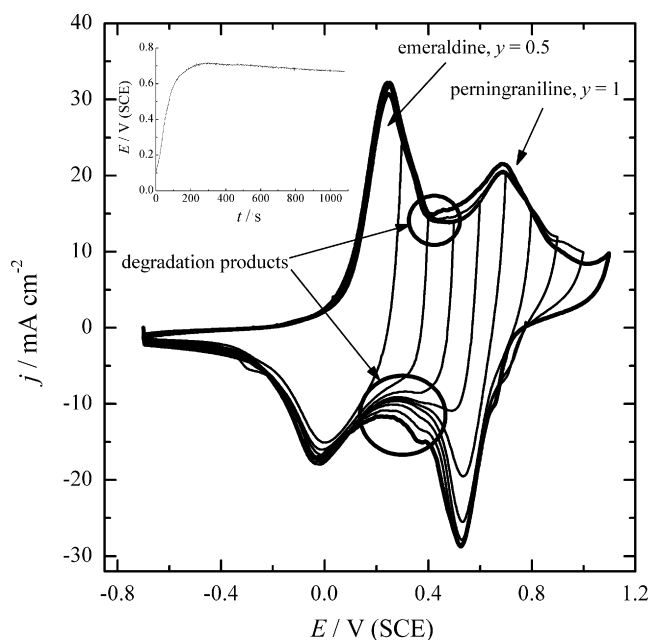


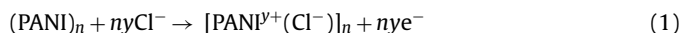
Fig. 1. Cyclic voltammograms of PANI electrode in 0.5 mol dm^{-3} HCl for anodic potential limits from 0.3 to 1.1 V (SCE), $\nu = 20 \text{ mV s}^{-1}$. Inset: Galvanostatic curve of electrochemical polymerization of aniline at graphite electrode in 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} , $j = 2.0 \text{ mA cm}^{-2}$.

water, and transferred into electrochemical cell containing 0.5 mol dm^{-3} HCl for further characterization. After transfer, before experiments, electrode was conditioned at potential of -0.7 V for 600 s to be completely discharged, and two cyclic voltammograms to the specified anodic potential limit was recorded, to obtain reproducibility.

All experiments were performed in standard three compartment electrochemical cell at ambient temperature (22°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

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 s is given in insert of Fig. 1. Electrochemical polymerization of aniline occurs together with insertion of chloride ions (doping) according to the equation:



where y is doping degree, defined as ratio between the number of charges in the polymer and the number of monomer units.

In order to investigate the influence of the potential on degradation of PANI, cyclic voltammograms ($\nu = 20 \text{ mV s}^{-1}$) of the PANI electrode were recorded for different anodic potential limits (starting from 0.3 V) in the potential range between -0.7 and 1.1 V (SCE), as shown in Fig. 1.

First anodic peak occurring at potential of about 0.25 V could be connected to doping of chloride anions via transition of leucoemeraldine form of PANI to emeraldine salt, while further increase of the potential above 0.50 V denotes transition of emeraldine salt to pernigraniline salt [17]. Between these two well defined anodic peaks, small peak at potential of about 0.45 V could be assigned to degradation reaction of PANI [17,18]. Different forms of PANI oxidation states are schematically represented in Fig. 2 [17]. Leucoemeraldine is fully reduced form with doping degree, $y = 0$, emeraldine salt is half oxidized form ($y = 0.5$), while pernigraniline salt refers to fully oxidized form ($y = 1$).

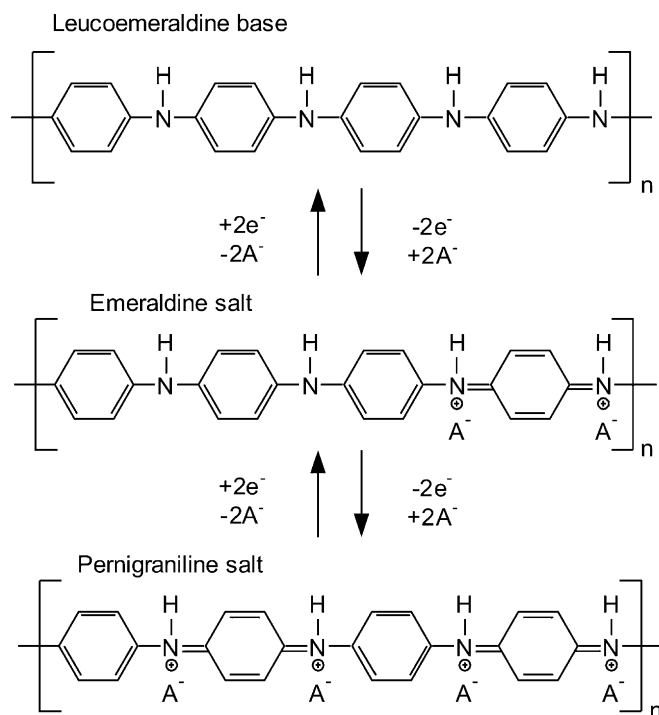


Fig. 2. Generalized scheme of electrochemical reactions of various PANI oxidation forms.

Fig. 3 shows deconvolution of stable cyclic voltammogram using Lorentzian peak fit functions for the proposed forms of the PANI electrode, and for anodic potential limit of 1.0 V. As it could be seen in Fig. 3, three well defined redox peaks (marked with 1, 2 and 3) were observed. First redox peak (marked with 1 and 1') could be attributed to emeraldine salt, second peak (2 and 2') is connected to formation and reduction of degradation products, third peak (3 and 3') refers to redox of pernigraniline forms, and fourth not well defined peak (4 and 4') could be connected to further degradation

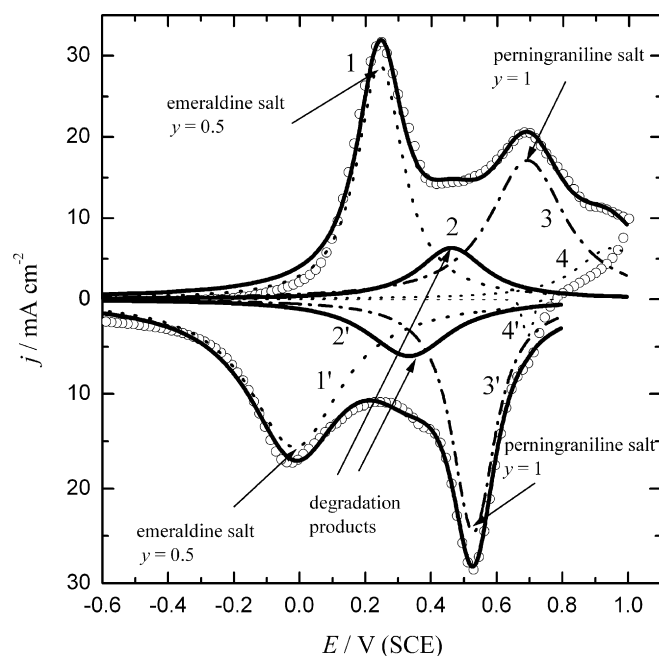


Fig. 3. Decoupling of the cyclic voltammogram in Fig. 2 for the potential limit of 1.0 V.

Table 1

Characteristic values of the current peaks obtained by deconvolution of the cyclic voltammogram given in Fig. 2.

Peak	E (V) (SCE)	q (mAh cm ⁻²)	q/q_{total}	j_p (mA cm ⁻²)
1	0.244	0.10389	0.37588	29.7
2	0.458	0.03306	0.11961	6.18
3	0.692	0.10569	0.38239	17.3
4	0.946	0.03347	0.12109	6.14
Total	–	0.27639	0.99897	–
1'	-0.0144	0.11639	0.48664	15.73
2'	0.333	0.03944	0.16414	6.05
3'	0.529	0.08264	0.34393	25.48
4'	0.695	0.00215	0.00894	5.76
Total	–	0.24028	1.00035	–

and reduction of degradation products of PANI [19]. Deconvolution of cyclic voltammogram provide possibilities for determination of potentials and current densities of each peak maximum (as indicated in Fig. 3), as well as the calculation of the corresponding charges for different forms of PANI, as summarized in Table 1.

Comparing the results presented in Table 1 it could be concluded that during charging and discharging of the PANI electrode, some small extent of the capacity was permanently lost, which is probably the consequence of PANI degradation. The main degradation products appear to be soluble benzoquinone, while other insoluble degradation products including PANI strands containing quinoimine end-groups and *ortho*-coupled polymers [20] are likely to remain on the electrode surface.

Since the state of emeraldine salt ($y \approx 0.5$) was accomplished at potential limit of 0.5 V, for the freshly prepared PANI electrode obtained by the same procedure, reproducible cyclic voltammograms in 0.5 mol dm⁻³ HCl at different scan rate (starting from 100 mV s⁻¹) and that anodic potential limit was given in Fig. 4.

By integration of anodic and cathodic part of the cyclic voltammogram (Fig. 4), the dependences of charge (doping) and discharge (dedoping) capacity on the scan rate were obtained and presented

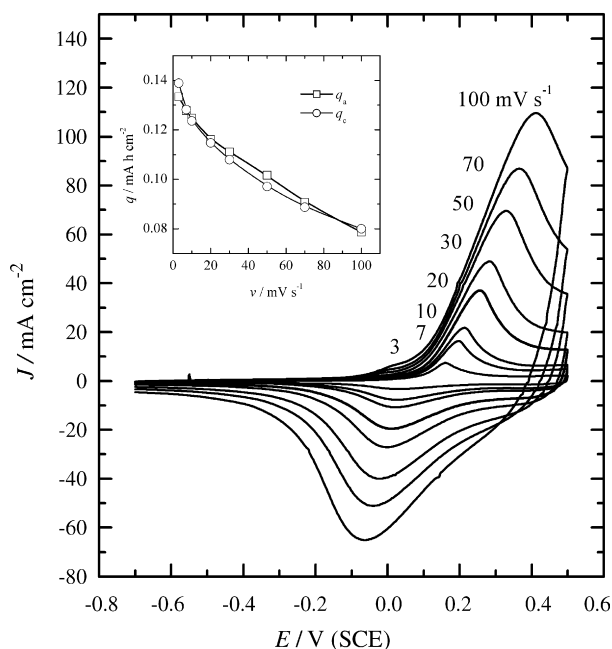


Fig. 4. Cyclic voltammograms of the PANI electrode in 0.5 mol dm⁻³ HCl, at different scan rate (as marked in figure). Insert: Dependence of (□) charge and (○) discharge capacity on scan rate.

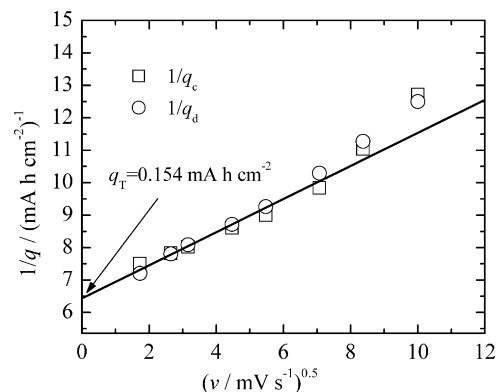


Fig. 5. The dependences of the reciprocal values (□) charge and (○) discharge capacity on square root of the scan rate.

in insert of Fig. 4. The electrode capacity was strongly dependant on scan rate. Possible explanation could be related to the fact that exchange of the chloride ions was hampered trough the pores of the PANI film. The dependences of the reciprocal values of the charge and discharge capacity on square root of the scan rate were linear, as shown in Fig. 5, so, it could be concluded that diffusion of chloride anions through the pores of the PANI film was really limiting factor [21].

The overall charge capacity of 0.154 mAh cm⁻² for the PANI electrode in stationary state conditions for the anodic potential limits of 0.5 V, was obtained by extrapolation of the linear dependences at $v \rightarrow 0$.

Based on available data, ratio of polymerized and active mass of the PANI electrode could be calculated. As seen in the insert of Fig. 1, polymerization of aniline at graphite electrode occurred at potential of about 0.7 V, which corresponds to formation of PANI in the form of pernigraniline salt ($y = 1$). Assuming that current efficiency of the polymerization process was 100% theoretical polymerized mass of the PANI electrode could be calculated using equation [22]:

$$m = \frac{jt(M_m + yM_a)}{(2 + y)F} \quad (2)$$

where m (g) is the mass of PANI, j (A) polymerization current density, t (s) polymerization time, M_m and M_a are molar mass of aniline monomer (93 g mol⁻¹) and chlorine anion (35.5 g mol⁻¹), $F = 96500$ As mol⁻¹ is Faraday constant and y is the doping degree. For the current density of 2 mA cm⁻² and polymerization time of 1080 s and taking $y = 1$ (pernigraniline salt), it could be calculated that the mass of PANI on graphite electrode is about 1 mg cm⁻². On the other hand, taking into account determined overall capacity of 0.154 mAh cm⁻² for emeraldine salt ($y = 0.5$), the active mass of PANI was calculated to be 0.25 mg cm⁻², meaning that only 25% of the theoretical mass is available for dopant exchange.

Charge/discharge curves of PANI electrode during ten cycles in 0.5 mol dm⁻³ HCl for current density of 1.0 mA cm⁻² are shown in Fig. 6, while Insert (a) of Fig. 6 shows charge/discharge capacities over cycle number and Insert (b) shows cyclic voltammograms taken before and after 1st, 5th and 10th cycle.

Charge of the PANI electrode was limited to the potential of 0.5 V to avoid higher transition of emeraldine salt to pernigraniline salt. Discharge of the PANI electrode was limited to potential of -0.6 V, to prevent hydrogen evolution reaction.

As it could be seen in Fig. 6 during charge, open circuit potential was -0.1 V, followed by sharp increase of the potential to 0.05 V. Further increase of the potential in the potential range between 0.1 and 0.5 V was almost linear and could be connected to transition of leucoemeraldine to emeraldine salt, and increase of the doping

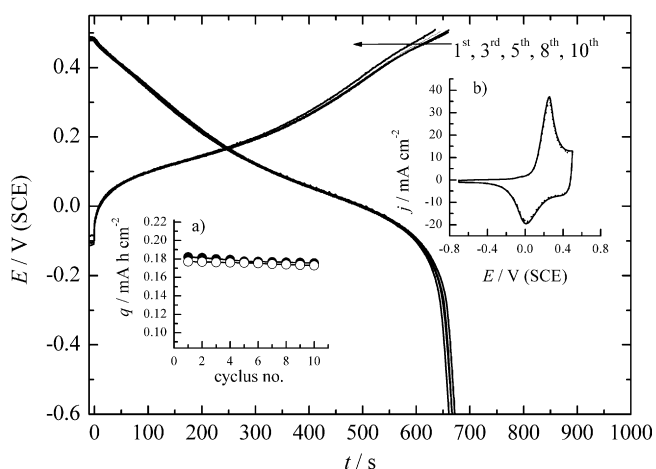


Fig. 6. Charge–discharge curve of PANI electrode at constant current density of 1.0 mA cm^{-2} in 0.5 mol dm^{-3} HCl. Insert (a) dependence of (●) charge and (○) discharge capacities on cycle number. Insert (b) cyclic voltammograms before and after 1st, 5th and 10th cycle.

degree from $y > 0$ to $y \approx 0.5$. Discharge of the electrode occurs in the potential range between 0.45 and -0.15 V , followed by fast decrease of the potential as a consequence of diffusion limitation. During 10 cycles the capacity was almost constant as it could be seen in Insert (a), meaning that there was practically no degradation of PANI for chosen charge/discharge potential limits. Cyclic voltammograms taken before and during cyclization are identical, as it could be seen in Insert (b) of Fig. 6, confirming that degradation of the PANI electrode was not observed for that potential region. The possible explanation could be connected to the fact that some forms of PANI are potential dependant and pH dependant [23]. Hence, at such low pH, extent of the degradation products was negligible and practically had no influence on charge/discharge characteristics of the PANI electrode during initial cyclization. However, this work is still in progress, in further studies it would be beneficial to investigate the influence of pH and anions on degradation of PANI during prolonged cyclization.

4. Conclusion

Electrochemical polymerization of PANI on graphite electrode from aqueous solution of 1.0 mol dm^{-3} HCl containing 0.25 mol dm^{-3} aniline was successively performed galvanostatically

from solution of hydrochloric acid containing aniline. The determined overall charge capacity of the PANI electrode in stationary state conditions was $0.154 \text{ mAh cm}^{-2}$. The active mass of the PANI electrode was calculated to be 25% of the overall polymerized mass, meaning that only 25% of the mass was available for the dopant exchange. Based on electrochemical studies, it was concluded that at potentials above 0.5 V , degradation of PANI occurred, so this potential was set as limit for electrode charging. During initial cyclization, charge/discharge capacity remained practically constant, indicated that PANI could be considered for potential use as electrode material in aqueous based rechargeable electrochemical power sources.

Acknowledgment

This work is financially supported by the Ministry of Science, Republic of Serbia, No. 142044.

References

- [1] A. Malinauskas, J. Malinauskienė, A. Ramanavičius, *Nanotechnology* 16 (2005) R51.
- [2] T.A. Skotheim, *Handbook of Conducting Polymers I*, Marcel Dekker, New York, 1986.
- [3] M. Sima, T. Visan, M. Buda, *J. Power Sources* 56 (1995) 133.
- [4] J. Kan, H. Xue, S. Mu, *J. Power Sources* 74 (1998) 113.
- [5] M.S. Rahmanifar, M.F. Mousavi, M. Shamsipur, M. Ghaemia, *J. Power Sources* 132 (2004) 296.
- [6] H. Karami, M.F. Mousavi, M. Shamsipur, *J. Power Sources* 117 (2003) 255.
- [7] B.Z. Jugović, T.Lj. Trišović, J. Stevanović, M. Maksimović, B.N. Grgur, *J. Power Sources* 160 (2006) 1447.
- [8] B.Z. Jugović, T.Lj. Trišović, J. Stevanović, M. Maksimović, B.N. Grgur, *Electrochim. Acta* 51 (2006) 6268.
- [9] M.S. Rahmanifar, M.F. Mousavi, M. Shamsipur, H. Heli, *Synth. Met.* 155 (2005) 480.
- [10] A. Mirmohseni, R. Solhjo, *Eur. Polym. J.* 39 (2003) 219.
- [11] R. Mažeikiene, A. Malinauskas, *Mater. Chem. Phys.* 83 (2004) 184.
- [12] P. Rüetschi, *J. Power Sources* 42 (1993) 1.
- [13] F. Beck, P. Rüetschi, *Electrochim. Acta* 45 (2000) 2467.
- [14] Lj.D. Arsov, W. Plieth, G. Koßmehl, *J. Solid State Electrochem.* 2 (1998) 355.
- [15] H.N. Dinh, J. Ding, S.J. Xia, V.I. Birss, *J. Electroanal. Chem.* 459 (1998) 45.
- [16] D.E. Stilwell, S.M. Park, *J. Electrochem. Soc.* 13 (1988) 2491.
- [17] N. Gospodinova, L. Terlemezyan, *Prog. Polym. Sci.* 23 (1998) 1443.
- [18] J.Y. Lee, L.H. Ong, G.K. Chuah, *J. Appl. Electrochem.* 23 (1993) 1031.
- [19] D.E. Stilwell, S.M. Park, *J. Electrochem. Soc.* 13 (1988) 2497.
- [20] A.Q. Zhang, C.Q. Cui, J.Y. Lee, *Synth. Met.* 72 (1995) 217.
- [21] K. Ghanbaria, M.F. Mousavi, M. Shamsipur, H. Karami, *J. Power Sources* 170 (2007) 513.
- [22] J. Kankare, in: D. Wise, G.E. Wnek, D.J. Trantolo, T.M. Cooper, J.D. Gresser (Eds.), *Electrical and Optical Polymer Systems: Fundamentals, Methods, and Applications*, Marcel Dekker, New York, 1998, p. 167.
- [23] S. Tawde, D. Mukesh, J.V. Yakhmi, *Synth. Met.* 125 (2002) 401.