[1.] M. M. GVOZDENOVIĆ, [2.] B. Z. JUGOVIĆ, [3.] T.LJ. TRIŠOVIĆ, [4.] J. S. STEVANOVIĆ,
[5.] M. V. PLAZINIĆ, [6.] B. N. GRGUR

ELECTROCHEMICAL CHARACTERISTICS OF POLYANILINE|LEAD-DIOXIDE POWER SOURCE

[1,5.] FACULTY OF TECHNOLOGY AND METALLURGY, UNIVERSITY OF BELGRADE, KARNEGIJEVA 4, 11120 BELGRADE, SERBIA
[2,3.] INSTITUTE OF TECHNICAL SCIENCE, SERBIAN ACADEMY OF SCIENCE AND ARTS, KNEZ MIHAJLOVA 35, 11000 BELGRADE, SERBIA
[4.] CEH-INSTITUTE OF CHEMISTRY, TECHNOLOGY AND METALLURGY, UNIVERSITY OF BELGRADE, NJEGOŠEVA 4, 11000 BELGRADE, SERBIA
[6.] TECHICAL FACULTY ČAČAK, UNIVERSITY KRAGUJEVAC, SVETOG SAVE 65, 32000 ČAČAK, SERBIA

ABSTRACT: Polyaniline (PANI) anode, electrochemically formed on graphite from aniline containing sulfuric acid solution, and electrochemically formed thin film lead dioxide cathode, were investigated for possible applications as electrode materials in PANI /H_2SO_4 /PbO_2 aqueous based rechargeable power sources. The stimulation of charge/discharge characteristics of the cell, based on half cell reactions investigations, was evaluated. Charging of the cell would occur in the voltage range of 1.20 and 1.70 V, while discharge is expected in the voltage range of 1.35 and 1.00 V.
KEYWORDS: polyaniline, lead dioxide, electrochemical power sources

INTRODUCTION

The determining factors of an electrochemical power sources success are often recognized as "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) [1, 2].

Electrochemical power sources systems composed of electroconducting polymers (ECP), metals (Pb, Zn, Al, Mg) and aqueous electrolytes are likely to meet most of these demands. The unique properties of ECP such as: mechanical strength, electrical conductivity, high energy and power density compared to classical inorganic compounds, possibility of reversible exchange of ions etc., permitted them to be considered as possible electrode materials for electrochemical power sources [3].
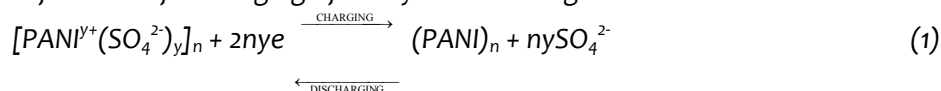
ECP can be obtained using both chemical and electrochemical oxidative polymerization. However, electrochemical synthesis is favorable, permitting synthesis without oxidizing agent followed by doping with inorganic or organic ions in a single step [4].
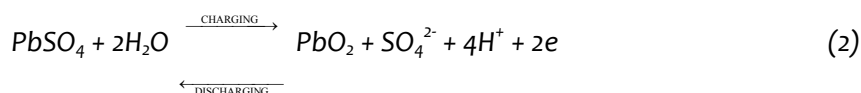
Among numerous ECP only few have been investigated for possible application in electrochemical power sources. Since the price of aniline monomer is scientifically lower comparing to other monomers, power sources based on polyaniline (PANI) metals (mainly zinc) and aqueous electrolytes are the most investigated systems [5-10].

Even the characteristics of these systems are principally very good, this type of electrochemical power sources have not been commercialized. The main reason is connected to degradation of PANI [11,12].

Lead acid batteries (Pb | PbO_2) are the first discovered and although they have lot of problems in exploitation, up to now they are the most large-scale electrochemical power sources. The problems in exploitation are mainly connected to negative Pb electrode, such as: dendrite formation provoking short circuit breakdown of the battery, passivation of the Pb electrode due to formation of inactive $PbSO_4$, water loss due to hydrogen evolution, etc. The use of PANI instead of Pb as negative electrode could overcome some of the mentioned problems. On the other hand, due to much smaller mass of PANI electrode, the specific energy and specific power could be significantly increased comparing to classical Pb | PbO_2 systems. The advantage of such power sources could be better ecological acceptance as a result of much smaller lead content and lower sulfuric acid concentration. It is interesting to note that after earlier works reported by Sima et al. [7], there are no studies concerning the use of PANI in lead acid power sources. Hence, the aim of this work is to investigate electrochemically synthesized PANI on graphite, as anodic material, and electrochemically synthesized lead dioxide as cathode for possible use in PANI /H_2SO_4 /PbO_2 rechargeable power sources.

In such system, the half reaction for charging of the system can be given as:

$$[PANI^{y+}(SO_4^{2-})_y]_n + 2nye \xrightarrow{\text{CHARGING}} (PANI)_n + nySO_4^{2-} \qquad (1)$$
$$\xleftarrow{\text{DISCHARGING}}$$

$$PbSO_4 + 2H_2O \xrightarrow{\text{CHARGING}} \xleftarrow{\text{DISCHARGING}} PbO_2 + SO_4^{2-} + 4H^+ + 2e \qquad (2)$$

where y refers to doping degree (ratio between the number of charges in the polymer and the number of monomer units). Is important to note that in fully charged PANI /H₂SO₄ /PbO₂ rechargeable power source PANI is in its dedoped form.

EXPERIMENTAL

PANI electrode was formed by anodic polymerization from aqueous solution of 1.1 mol dm^{-3} H$_2$SO$_4$ and 0.2 mol dm^{-3} aniline at constant current density of 2.5 mA cm^{-2} on graphite (S = 0.64 cm^2). Prior to use, aniline (p.a. Aldrich) was distilled in argon atmosphere. Cylindrically shaped graphite electrode was first mechanically polished with fine emery papers (2/0, 3/0 and 4/0) and then with polishing alumina (1μm Banner Scientific Ltd.) on polishing cloths (Buehler Ltd.). After mechanical polishing, the traces of the polishing alumina were removed from the electrode surface in ethanol using ultrasonic bath during 5 min. After polymerization, PANI electrode was dedoped with current density of 1.25 mA cm^{-2}, washed with distilled water and then investigated in 1.1 mol dm^{-3} H$_2$SO$_4$. The lead dioxide electrode (PbO$_2$) was prepared from pure 99.95 % lead, according to established Planté formation procedure described by Peterson et al [13,14].

All experiments were carried out in three compartment electrochemical cells at ambient temperature (22°C). Saturated electrode (SCE) served as reference, while platinum foil (S = 2 cm^2) was used as counter electrode. The measurements were carried out using PAR 273A potentiostat/galvanostat interfaced to PC.

RESULTS AND DISCUSSION. CHARACTERIZATION OF PANI ELECTRODE

In Fig. 1 charge/discharge (doping/dedoping) curves of the PANI electrode for different current densities of: 0.50 – 1.25 mA cm^{-2} and anodic potential limit of 0.32 V in 1.1 mol dm^{-3} H$_2$SO$_4$ are shown. Anodic potential limit was chosen bearing in mind that at potentials higher than 0.35 V degradation of PANI is expected [11,12].

Charging of the electrode started at potential of ~ 0.05V while discharging occurred in the potential range between 0.3 and – 0.3 V. Charging capacity, as seen in insert of Fig. 1., is independent on current density, while discharging capacity decreases with increasing current density. For current densities below 1.25 mA cm^{-2}, columbic efficiency is higher than 100 %. This observation could be connected to possibilities of hydrogen evolution and protonization of emeraldine form of PANI at negative potentials and low current densities [11,12]. This additional charge is easily discharged at open circuit potentials and has no contribution in further charging. Since the columbic efficiency of nearly 100 % was achieved with current density of 1.25 mA cm^{-2}, for further investigation of cyclic characteristic of the PANI electrode this charge/ discharge current was used.

Initial cycling characteristics of PANI electrode obtained with constant current density of 1.25 mA cm^{-2} during 15 cycles is given in Fig. 2. Since, the degradation of PANI is expected at the potentials above ~ 0.35 V, in order to investigate the influence of degradation, the cycling potential limit for charging of the electrode was extended to 0.45 V for charging and -0,6 V for discharging.

As it can bee seen from Fig. 2. charge/discharge curves remained practically the same during fifteen cycles, with almost constant values of the electrode charging and discharging capacity, with columbic efficiency of ~ 95 %. Based on obtained results, it could be concluded that in during initial cyclization in investigated potential range degradation of PANI could be neglected, but, based on
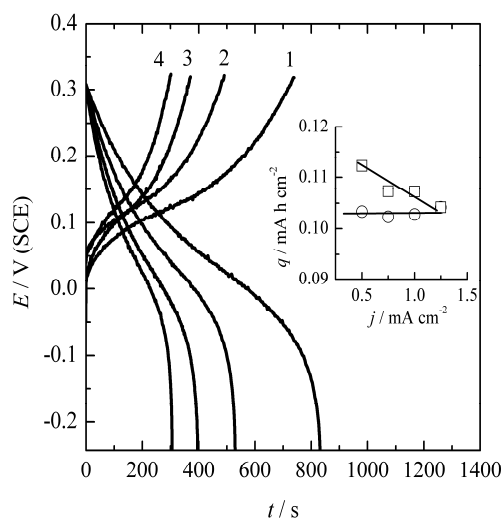

Fig. 1. Charge/discharge curves of PANI electrode in 1.1 mol dm^3 H$_2$SO$_4$, where the numbers in the figure refer to different current densities as: 1)-0.50, 2)-0.75, 3)-1.00 and 4)-1.25 mA cm^{-2}.
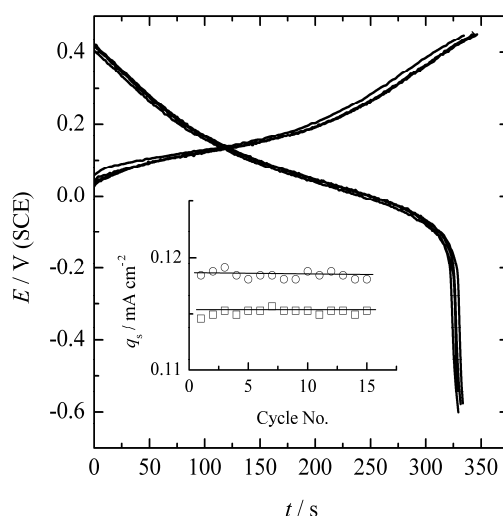Insert: Dependences of: (○)-charge and (□)-discharge capacity on current density

Fig. 2. Cycling characteristics of PANI electrode in 1.1 mol dm^3 H$_2$SO$_4$ at conctant current density of 1.25 mA cm^{-2}. Insert: Dependences of (○)-charge and (□)-discharge capacity on cycle number

literature data[11,12], it is possible to be expected to occur during prolonged cyclization, therefore it is recommended that the optimal potential limit for charging of PANI electrode should not exceed 0.35 V.

CHARACTERIZATION OF PbO₂ ELECTRODE

In order to investigate discharge characteristics of electrochemically formed PbO₂ electrode [11,12], the following procedure was applied. Electrode was always charged with current density of 2 mA cm⁻² during 500 s, and then discharged with current densities between 1 and 4 mA cm⁻² as seen in Fig. 3. Based on discharging times, the dependences of columbic efficiency and discharge capacity on applied current density were calculated and given in insert of Fig. 3.

For lower current densities of 1.0 and 2.0 mA cm⁻² columbic efficiency is ~ 85 %, while current efficiency and discharge capacity decrease for higher current densities, probably as a result of diffusion limitations. Thus, for further investigation discharge current of 2 mA cm⁻² was used.

In order to investigate initial cyclic characteristic, PbO₂ electrode was submitted to fifteen charge/discharge cycles in 1.1 mol dm⁻³ H₂SO₄ with current density of 2.0 mA cm⁻² and results are presented in Fig. 4.

As it can been seen from Fig. 4, during fifteen cycles charge/discharge capacity has practically constant values, with constant columbic efficiency of ~ 85 %. These findings suggest that electrochemically formed PbO₂ electrode accomplishes demands for potential application in PANI/H₂SO₄/PbO₂ electrochemical power sources.

SIMULATION OF PANI/H₂SO₄/PbO₂ POWER SOURCE CHARACTERISTICS

Based on charge /discharge characteristics of PANI and PbO₂ electrodes necessary data for estimation of the possible characteristics of PANI|PbO₂ power source are given in Fig.5.

Fig.3. Discharge characteristics of PbO₂ electrode in 1.1 mol dm⁻³ H₂SO₄, where the numbers in the figure refer to different current densities as:1)-1.0, 2)-2.0, 3)-3.0 and 4)-4.0 mA cm⁻².
Insert: Dependences of columbic efficiency and discharge capacity on discharge current density.

Fig.4. Cycling characteristics of PbO₂ electrode in 1.1 mol dm⁻³ H₂SO₄ at constant current density of 2.0 mA cm⁻²
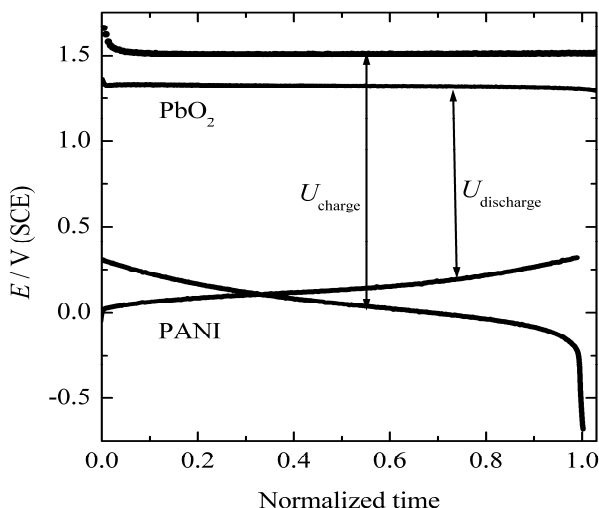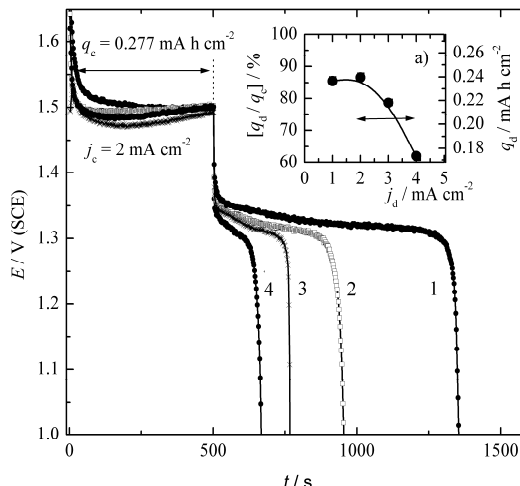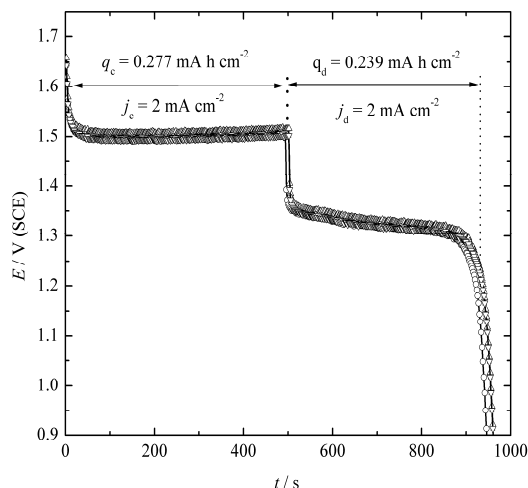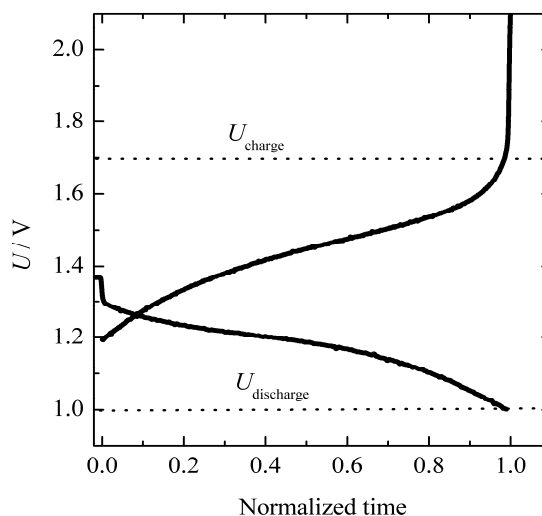

Fig. 5. Charge/discharge curves used for estimation of the possible characteristics of PANI|PbO₂ rechargeable power source

The possible voltage characteristics of PANI /H₂SO₄ /PbO₂ rechargeable power source system were done for anodic current density of 1 mA cm⁻² (PANI electrode) and cathodic current density

Fig.6. Possible voltage characteristics of PANI|PbO₂ rechargeable power source

of 2 mA cm^{-2} (PbO$_2$ electrode), assuming that at low current densities voltage loss resulted from additional ohmic drops can be neglected, and that PANI electrode was formed on carbon support with low roughness factor of 2. Obtained results are presented in Fig. 6.

As it can bee seen in Fig. 6 charging of PANI /H$_2$SO$_4$ /PbO$_2$ system would occur in the voltage range between 1.2 and 2.1, but since there is no additional charge above 1.7 V, system should be charged only to that voltage, charging of the system above 2V could provoke hydrogen evolution reaction. After charging open circuit voltage is ~1.35 V similar to metal hydride cells. Discharge of the system would occur in the voltage range between 1.35 and 1.0 V. For the discharge voltage below 1.0 V, corresponding to the PANI doping potentials of 0.32 V, the possibilities of PANI degradation are not excluded, so it is recommended that system should be discharge to 1.0 V.

CONCLUSIONS

In the light of mentioned "three E" criteria, electrochemical rechargeable power sources based on PANI anode and lead dioxide cathode have some advantages comparing to classical Pb|PbO$_2$ systems, such as: much lower lead content and electrolyte concentration, easier manufacturing demands, ecological acceptability, and possibility of avoiding some problems connected to Pb electrode. Disadvantages of this systems comparing to commercial Pb|PbO$_2$ are in the first place, connected to smaller discharge voltage and relatively small PANI electrode capacity. Therefore, further investigations of PANI synthesis on high surface are materials or powered PANI carbon composites are required in order to increase the specific active mass of the PANI anode. On the other hand, determination of the cycle life of PANI /PbO$_2$ rechargeable power sources in real conditions would be the most important parameter in further testing.

Acknowledgment

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