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Characteristics of polyaniline lead - dioxide power sources

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ABSTRACT:

Polyaniline (PANI) anode, electrochemically synthesized on graphite electrode from 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 1.2 and 1.7 V, while discharge would occur in the range of 1.3 and 1 V.

Key words: polyaniline, lead dioxide, power sources

INTRODUCTION:

Electroconducting (ECP) polymers due to their specific properties such as: low specific weight compared to classical inorganic compounds, high energy and power density and ability of reversible exchange of ions, have gained much attention as possible electrode materials in electrochemical power sources. The determining factors of a battery system are recognized as “three E criteria” (energy, economics, environment), which are likely to be accomplished in systems based on ECP, metals and aqueous electrolytes[1]. Among numerous ECP, up to now only few of them has been investigated for possible use in electrochemical power sources. The most extensively investigated systems are based on polyaniline (PANI) combined to electronegative metals. In this work electrochemically synthesized PANI on graphite, as anodic material, and electrochemically synthesized lead dioxide as cathode were investigated for possible application in PANI$|H_2SO_4|PbO_2$ rechargeable power sources. In such system, the half reaction for charging of the cell can be given as:

$$[PANI^{y+}(SO_4^{2-})_y]_n + 2nye \rightarrow (PANI)_n + nySO_4^{2-} \quad (1)$$

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e \quad (2)$$

Is important to note that in fully charged PANI$|H_2SO_4|PbO_2$ battery PANI is in its dedoped form.

EXPERIMENTAL: Polyaniline thin film electrode was formed by anodic polymerization from aqueous solution of 1.1 mol dm^{-3} H_2SO_4 and 0.2 mol dm^{-3}

aniline at constant current density of 2.5 mA cm^{-2} on graphite. Prior to use aniline (p.a. Aldrich) was distilled in argon. Cylindrically shaped graphite 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.). After mechanical polishing, the traces of alumina were removed from the electrode surface in ethanol using ultrasonic bath. After polymerization, PANI electrode was dedoped with current density of 1.25 mA cm^{-2}, washed with bidistilled water and than investigated in 1.1 mol dm^{-3} H_2SO_4. The lead dioxide electrode was prepared from pure 99.95 % lead, according to established Planté formation procedure described by Peterson et al.[2].
All experiments were carried out in three compartment electrochemical cells. Saturated electrode served as reference, while platinum foil (S = 2 cm^2) was used as counter electrode. Electrochemical measurements were performed using GMRY PC3 potentiostat controlled by computer.

RESULTS AND DISCUSSION:

Characterization of PANI electrode
In Fig. 1. charge/discharge curves of 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_2SO_4 are shown. Anodic potential limit was chosen bearing in mind that at potentials higher than 0.35 V degradation of PANI is expected[3]. Charging of the electrode starts at potential of ~ 0.05V and discharging 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 decrease 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 at negative potentials and low current densities. This additional charge is easily discharged at open circuit potentials and has no contribution in further charging

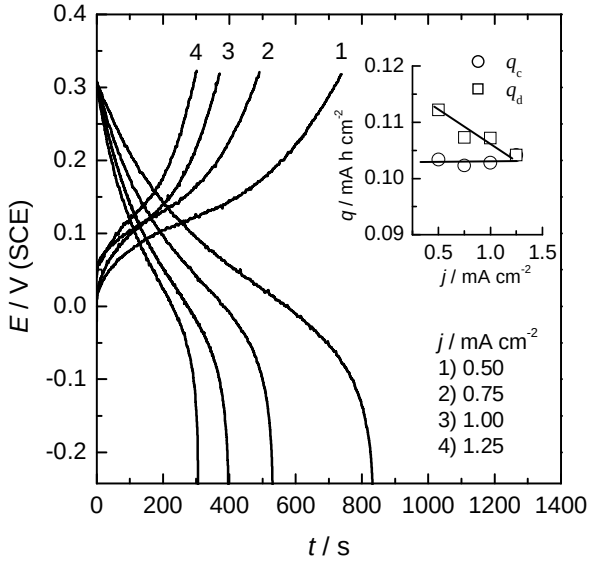

Fig.1. Charge/discharge curves of PANI electrode for different current densities in 1.1 mol dm^{-3} H_2SO_4. Insert: Charge/discharge capacity

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 possibly occurs above potentials of ~ 0.35 V, in order to investigate the influence of degradation, the cycling potential limits were extended to 0.45 V for charging and – 0.6 V for discharging[4].

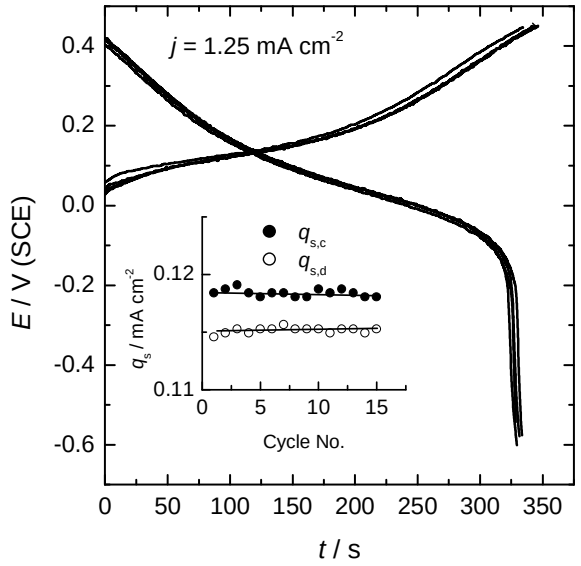

Fig. 2. Cycling characteristics of PANI electrode in 1.1 mol dm^{-3} H_2SO_4 at constant current density of 1.25 mA cm^{-2}. Insert: Dependence of the electrode capacity on cycle number

As it can bee seen from Fig. 2. charge/discharge curves are practicaly the same during fefteen cycles, with almost constant values of electrode charging and discharging capacity, with columbic efficiency of ~ 95 %. Based on obtained results, it could be concluded that in investigated potential range degradation of PANI didn't occur, but it is expected to occur during prolonged cycliztion, so it is recommended that the optimal potential limit for charging of PANI electrode should be ~ 0.35 V[4].

Characterization of PbO_2 electrode

In order to investigate discharge characteristics of electrochemically formed PbO_2 electrode[2], the following procedure was applied. Electrode was always charged with current density of 2 mA cm^{-2} during 500 s, and than 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.

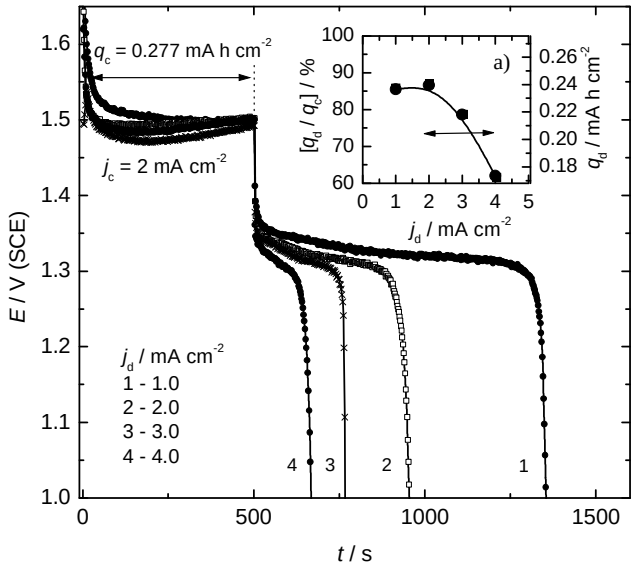

Fig. 3. Discharge characteristics of PbO_2 electrode in 1.1 mol dm^{-3} H_2SO_4 for different discharge current densities. Insert. Dependences of columbic efficiency and discharge capacity on discharge current density.

In order to investigate cyclic characteristic, PbO_2 electrode was submitted to fifteen charge/discharge cycles in 1.1 mol dm^{-3} H_2SO_4 with current density of 2.0 mA cm^{-2} and results are presented in Fig. 4.

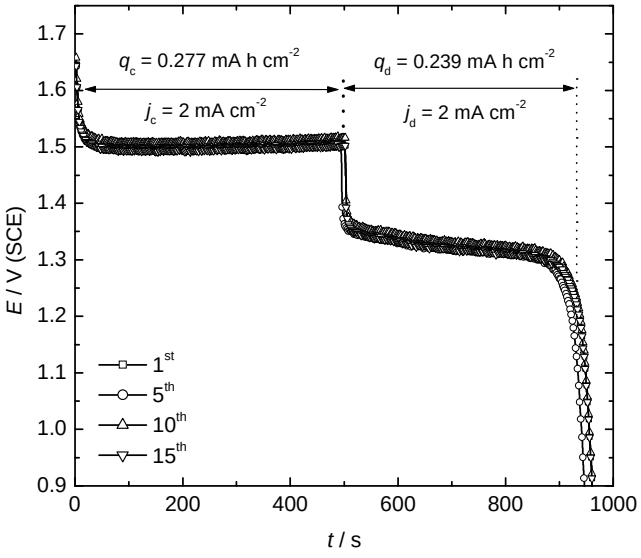

Fig. 4. Cycling characteristics of PbO_2 electrode in 1.1 mol dm^{-3} H_2SO_4 at constant current
density of 2.0 mA cm^{-2}

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 PbO_2 electrode accomplishes demands for potential application in PANI $|$ H_2SO_4 $|$ PbO_2 cell.

Possible characteristics of PANI /H_2SO_4 /PbO_2 power sources

Based on charge /discharge characteristics of PANI and PbO_2 electrodes (presented in Fig. 2. and Fig. 3.), simultation of the possible electrochemical characteristics of PANI $|$ H_2SO_4 $|$ PbO_2 cell were done for anodic current density of 1 mA cm^{-2} (PANI electrode) and cathodic current density of 2 mA cm^{-2} (PbO_2 electrode), assuming that for 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. 5.

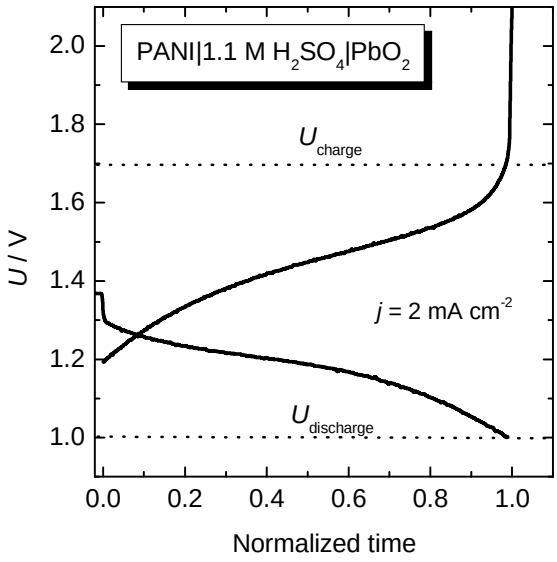

Fig. 5. Simultation of the possible electrochemical characteristics of PANI $|$ H_2SO_4 $|$ PbO_2 cell

As it can bee seen from Fig. 5. charging of the cell occurs 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. After charging open circuit voltage is ~ 1.35 V similar to metal hydride cells.

REFERENCES

1. P. Rüetschi, *J. Power Sources*, **42** (1993) 1
2. L. Peterson, B. Berghult, E. Ahlberg, *J. Power Sources*, **74** (1998) 68
3. N. Gospodinova, L. Terlemezyan, *Prog. Polym. Sci.*, **23** (1998) 1443
4. B. N. Grgur, V. Ristić, M. M. Gvozdenović, M. D. Maksimović, B. Z. Jugović *J. Power Sources,***180** (2008) 635

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