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Characteristics of polyaniline lead - dioxide power sources

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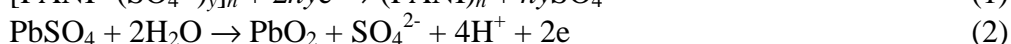
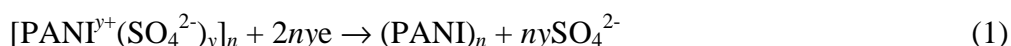
ABSTRACT:

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|H₂SO₄|PbO₂ 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 electrolytes¹. 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|H₂SO₄|PbO₂ rechargeable power sources. In such system, the half reaction for charging of the cell can be given as:



Is important to note that in fully charged PANI|H₂SO₄|PbO₂ 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 H₂SO₄ 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 ($1 \mu\text{m}$ 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 $1.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. 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 ($S = 2 \text{ cm}^2$) 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: $0.50 - 1.25 \text{ mA cm}^{-2}$ and anodic potential limit of 0.32 V in $1.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ are shown. Anodic potential limit was chosen bearing in mind that at potentials higher than 0.35 V degradation of PANI is expected³. Charging of the electrode starts at potential of $\sim 0.05 \text{ V}$ 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

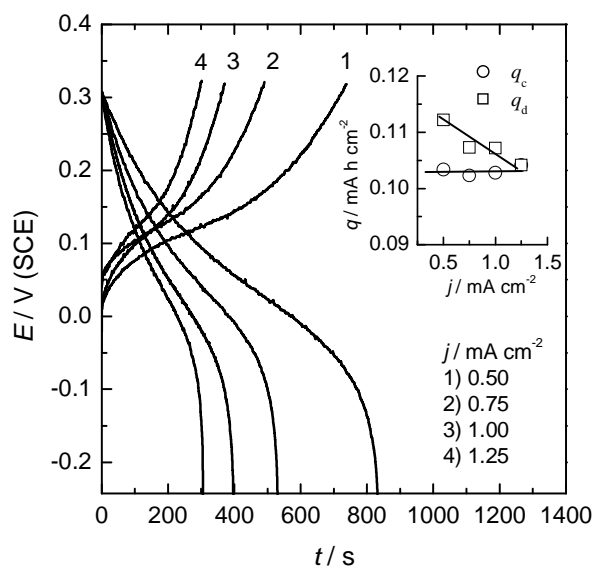


Fig.1. Charge/discharge curves of PANI electrode for different current densities in $1.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. Insert: Charge/discharge capacity

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 $\sim 0.35 \text{ V}$, 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 discharging⁴.

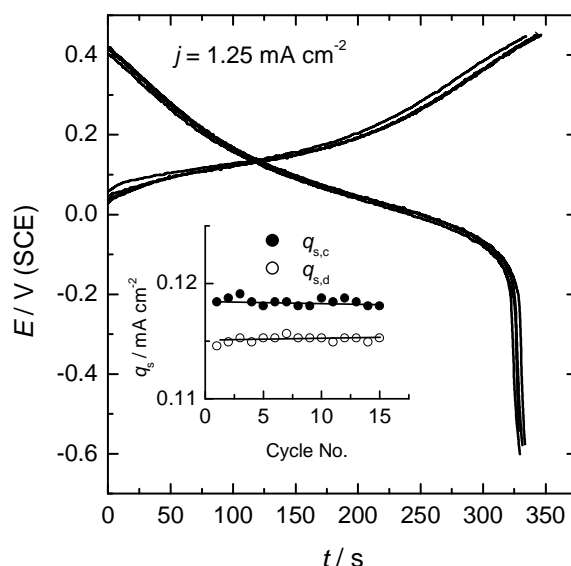


Fig. 2. Cycling characteristics of PANI electrode in $1.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at constant current density of 1.25 mA cm^{-2} . Insert: Dependence of the electrode capacity on cycle number

As it can be seen from Fig. 2. charge/discharge curves are practically the same during fifteen cycles, with almost constant values of electrode charging and discharging capacity, with coulombic efficiency of $\sim 95 \%$. 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 cyclization, so it is recommended that the optimal potential limit for charging of PANI electrode should be $\sim 0.35 \text{ V}$ ⁴.

Characterization of PbO_2 electrode

In order to investigate discharge characteristics of electrochemically formed PbO_2 electrode², 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 coulombic 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} coulombic efficiency is $\sim 85 \%$, 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.

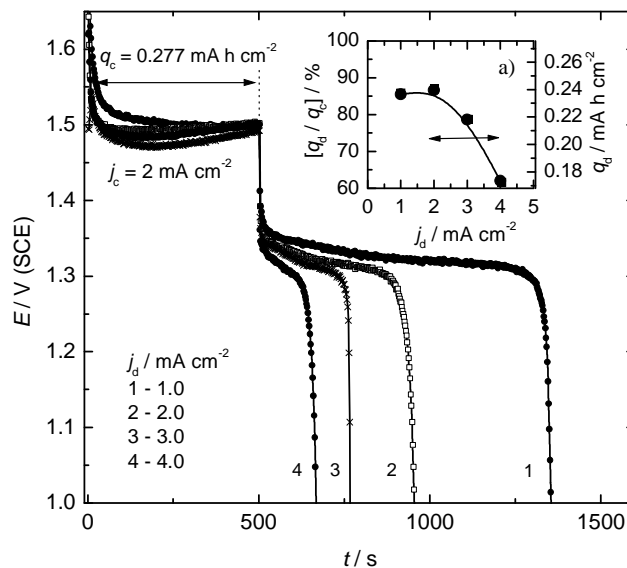


Fig. 3. Discharge characteristics of PbO₂ electrode in 1.1 mol dm⁻³ H₂SO₄ for different discharge current densities. Insert. Dependences of coulombic efficiency and discharge capacity on discharge current density.

In order to investigate 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.

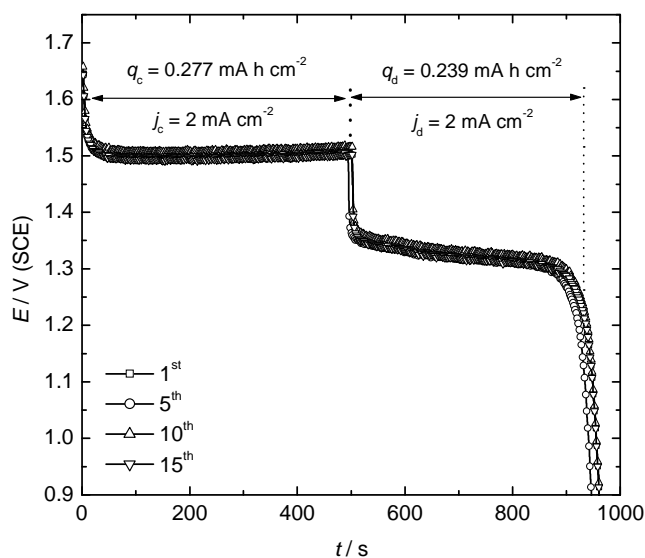


Fig. 4. Cycling characteristics of PbO₂ electrode in 1.1 mol dm⁻³ H₂SO₄ at constant current density of 2.0 mA cm⁻²

As it can be seen from Fig. 4., during fifteen cycles charge/discharge capacity has practically constant values, with constant coulombic efficiency of ~ 85 %. These

findings suggest that electrochemically formed PbO_2 electrode accomplishes demands for potential application in $\text{PANI} | \text{H}_2\text{SO}_4 | \text{PbO}_2$ cell.

Possible characteristics of $\text{PANI} / \text{H}_2\text{SO}_4 / \text{PbO}_2$ power sources

Based on charge /discharge characteristics of PANI and PbO_2 electrodes (presented in Fig. 2. and Fig. 3.), simulation of the possible electrochemical characteristics of $\text{PANI} | \text{H}_2\text{SO}_4 | \text{PbO}_2$ 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.

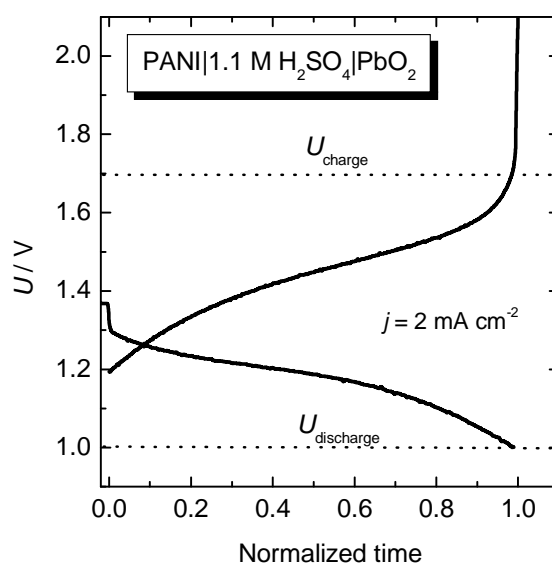


Fig. 5. Simulation of the possible electrochemical characteristics of $\text{PANI} | \text{H}_2\text{SO}_4 | \text{PbO}_2$ cell

As it can be 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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