



Short communication

Polyaniline as possible anode materials for the lead acid batteries

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ABSTRACT

Electrochemically formed thin film polyaniline (PANI) anode and lead dioxide (PbO₂) cathode, obtained from sulfuric acid solution, for potential applications as electrode materials in PANI|H₂SO₄|PbO₂ aqueous based rechargeable power sources, have been studied using cyclic voltammetry and galvanostatic techniques. Based on the investigations of half cell reactions, the simulation of the charge/discharge characteristic of the possible cell has been done.

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1. Introduction

Electrochemical properties of electroconducting polymers (ECP), due to their low specific weight when compared with classical inorganic compounds; high energy and power density and ability to reversible exchange counter ions, have stimulated the interest in their use as electrode materials of the electrochemical power sources [1]. According to Rüetschi, and elaborated by Beck and Rüetschi, determining factors of the battery system success are a 'three E' criteria: Energy (high energy content with respect to unit weight and volume), Economics (low manufacturing costs, low maintenance during use, long service life) and Environment (free of toxic materials, safe, low energy consumption during manufacture and use, long service life, high reliability, easy to recycle) [2,3].

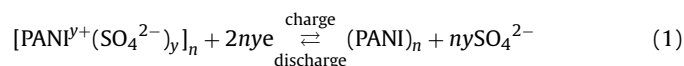
Electrochemical systems based on ECP, metals (e.g. Pb, Zn, Mg, Al) and aqueous based electrolytes have potentials to accomplish most of the three E criteria. Even, the variety of the ECP is very high, up to now only a few of them has been investigated and tested for the application in aqueous based electrochemical power sources. Polyaniline (PANI) combined with electronegative metals (mainly zinc) are the most extensively investigated systems [4–15]. This type of the electrochemical power sources has not been commercialized, even the electrochemical characteristics are in principles very good. The main reasons for this are degradation process of polyaniline electrode (used as cathode) at potentials more positive than ~0.5 V [16,17].

The lead acid batteries are one of the earlier discovered, and even due to the lot of problems in exploitation, up to now they are practically the most large-scale rechargeable electrochemical power systems. Some of the problems in exploitation have to be connected with behaviors of negative, Pb, electrode, like dendrite formation which can provoke short circuit breakdown of the cell, pasivation of the negative electrode due to the formation of PbSO₄ inactive film, water loss due to the hydrogen evolution reaction, etc.

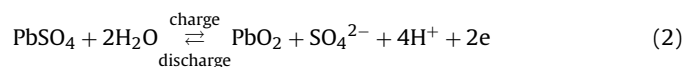
The use of ECP negative electrode could avoid some of the problems with negative Pb electrode in comparison with classical Pb|PbO₂ systems. In addition, the specific energy and specific power could increase significantly, due to the much smaller mass of PANI electrode when compared with classical Pb negative electrode. One more advantages of such cell would be better ecological acceptability due to the lower concentration of sulfuric acid, and much smaller lead contents.

It is interesting to note that after some earlier works on PANI, Pb and PbO₂ cells, as reported by Sima et al. [7], up to now practically there is no studies considering ECP|PbO₂ systems. Attempts to improve characteristics of the negative, Pb, electrode and prevent the grids corrosion with PANI coatings were conducted by Martha et al. [18,19].

In PANI|PbO₂ system, the half cell reaction for charge and discharge can be given as



where y is doping degree, and



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According to this scheme, it is important to note that during charge processes of PANI|PbO₂ cell, PANI will be dedoped, and during discharge PANI will be doped.

Hence, in this work the behavior of the electrochemically formed polyaniline and lead dioxide thin film electrodes for potential applications as electrode materials in PANI|H₂SO₄|PbO₂ aqueous based rechargeable power sources has been investigated.

2. Experimental

Thin film PANI electrode was synthesized from 1.1 M sulfuric acid solution with addition of 0.2 M aniline (ANI) monomer (p.a. Merck, previously distilled in argon atmosphere), at a constant current densities of 2.5 mA cm⁻² during 1440 s with the total polymerization charge of 1 mAh cm⁻². PANI electrode was synthesized on cylindrically shaped graphite electrode ($S = 0.64 \text{ cm}^2$) inserted in Teflon holder. After polymerization, PANI electrode was discharged with the current density of 1.25 mA cm⁻², washed with bidistilled water and transferred into the electrochemical cell with pure 1.1 M H₂SO₄ for further investigations. Before experiments in pure 1.1 M H₂SO₄ electrode was further discharged at -0.6 V during 180 s.

Lead dioxide electrode was prepared on cylindrically shaped pure lead (99.95%) inserted in Teflon holder ($S = 0.64 \text{ cm}^2$), according to the Planté formation process described in detail by Petersson et al. [20,21]. In order to remove naturally formed lead oxides in the air, the lead sample was dipped in 8 M HNO₃ for 30 s, and rinsed in deionised water before the electrode was immersed in the 0.5 M H₂SO₄ and 0.05 M KClO₄ (p.a. Merck) to start the formation process. The lead electrode was initially pretreated cathodically for 30 min at 1.5 mA cm⁻², and then oxidized and reduced galvanostatically in the same electrolyte at current densities of 2 mA cm⁻². After formation process, the remains of perchlorate ions were removed from the electrode by rinsing with deionised water. Finally, the PbO₂ electrode was completely oxidized in pure 1.1 M H₂SO₄ with the current density of 2 mA cm⁻² during 2000 s.

The working electrodes, prior to the experiments were mechanically polished with fine emery papers (2/0, 3/0 and 4/0, respectively) and then with polishing alumina of 1 μm (Banner Scientific Ltd.) on the polishing cloths (Buehler Ltd.). After mechanical polishing the traces of polishing alumina were removed from the electrode surface in ultra-sonic bath in ethanol during 5 min.

For all experiments three compartment electrochemical cells, with platinum foil ($S = 2 \text{ cm}^2$) as a counter and saturated calomel electrode, $E_r = 0.243 \text{ V}$ (SHE), as a reference electrode at room temperature (22 °C) were used.

The electrochemical measurements were carried out using GAMRY PC3 potentiostat controlled by a computer.

3. Results and discussion

3.1. Synthesis and characterization of polyaniline electrode

Fig. 1 shows synthesis and characterization of the PANI electrode. Insert of Fig. 1 shows the galvanostatic curve of aniline polymerization in 1.1 M H₂SO₄ and 0.2 M aniline monomer on graphite electrode at constant current density of 2.5 mA cm⁻² with the polymerization charge, q_{pol} , of 1 mAh cm⁻² (1440 s). With the higher polymerization current densities, due to the high polymerization potential more degradation products and lower current efficiency were obtained (see text below).

As it can be seen from the insert of Fig. 1, aniline polymerization in sulfuric acid solution proceed in the potential range between 0.7 and ~0.56 V according to the equation:

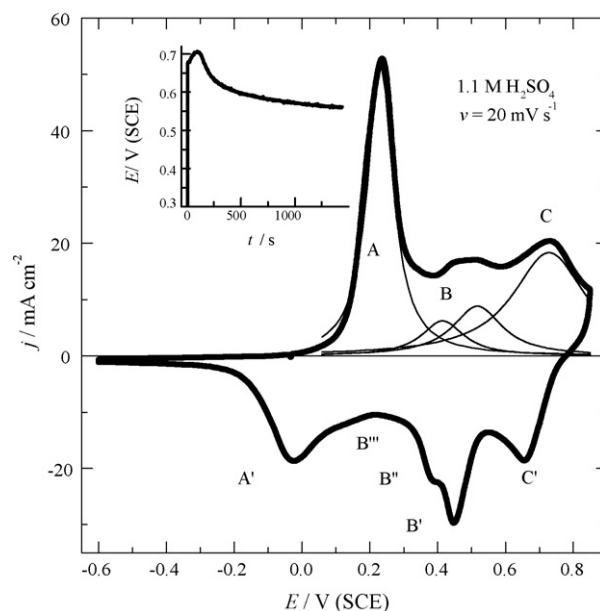
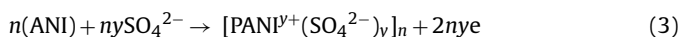


Fig. 1. Cyclic voltammogram (20 mV s^{-1}) of the PANI electrode in pure 1.1 M H₂SO₄. Insert: galvanostatic curve for polymerization of aniline in 1.1 M H₂SO₄ and 0.2 M aniline monomer on graphite electrode at the current density of 2.5 mA cm⁻².

Fig. 1 also shows cyclic voltammogram of the PANI electrode in pure 1.1 M H₂SO₄ for the anodic potential limit of 0.85 V. Full thick line represent experimental data, while thin lines represent peak deconvolution using Lorentzian peak fit function. Doping of the PANI electrode with sulfate anions starts at ~-0.1 V and proceed up to the potential of 0.85 V through different oxidation states. Appearance of well-defined peak at 0.22 V (peak A), due to the color changes from deep green to practically black, could be attributed to the changes of the doping degrees of emeraldine salt between $y > 0$ and 0.5. It should be noted that at low negative potentials leucoemeraldine form ($y \approx 0$) could exist as well [22]. Further oxidation of emeraldine salt to pernigraniline salt ($y = 0.5-1$) can be attributed to the peak C at potential higher than 0.5 V. Between those two main oxidation states, two peaks marked with B at ~0.45 V corresponds to the formation of the polyaniline degradation or hydrolysis products [17,23–25]. The main degradation product appears to be soluble benzoquinone with the redox of the benzoquinone/hydroquinone couple. Other inactive insoluble degradation products have been suggested to remain on the electrode surface, including PANI strands containing quinoneimine end groups [20,21] and *ortho*-coupled polymers [23].

In the cathodic scan reduction of pernigraniline salt (peak C'), degradation products (peaks B', B'' and B''') and emeraldine salt (peak A') proceeds in the potential range between 0.85 and -0.3 V. Considering the appearance of the degradation products at the potentials more positive than ~0.3 V, it should be suggested that PANI electrode in 1.1 M H₂SO₄ has to be doped maximally to the potential of approximately 0.35 V.

Doping–dedoping curves of PANI electrode for different current densities, and for doping potential limit of 0.32 V in 1.1 M H₂SO₄ are shown in Fig. 2. Doping of the electrode starts at ~0.05 V, while dedoping in the range between 0.3 and -0.3 V. As it can be seen from the insert of Fig. 2 doping electrode capacity was practically independent on the applied current density. On the contrary, dedoping electrode capacity was dependent on the current density, and decrease with increasing current density. Columbic efficiency, for the current density higher than 1.25 mA cm⁻² was ~95%, while for the current density smaller than 1.25 mA cm⁻² was higher than 100% (104–108%). These unusual results could be explained by the

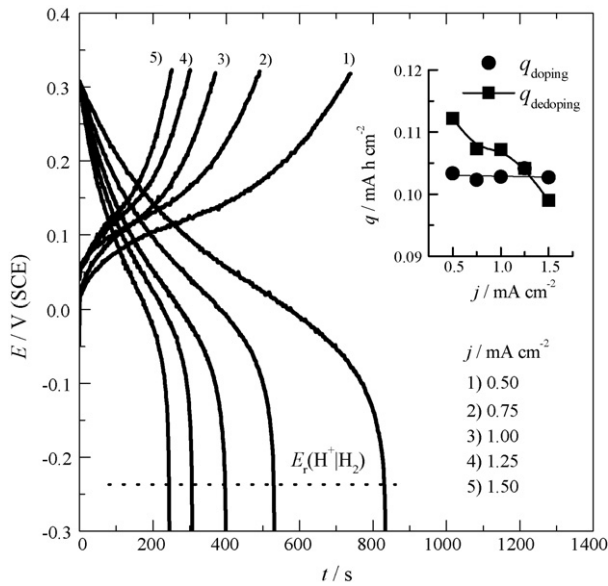


Fig. 2. Doping–dedoping curves of PANI electrode for the different current densities, and for the anodic potential limit of 0.32 V in 1.1 M H₂SO₄. Insert: dependence of electrode capacity on current density.

possibilities of hydrogen evolution reaction ($E_r = -0.24$ V) or more probably by formation of protonized emeraldine or leucoemeraldine at low current densities and negative potentials [22]. Such additional charge could be quickly discharged on the PANI electrode open circuit potentials of ~ 0 V after current was interrupted, and cannot be observed during doping. Since the current efficiency of 100% was obtained only with current density of ~ 1.25 mA cm⁻², this value was chosen for the further investigations.

The active mass of PANI electrode and the current efficiency of the polymerization process were estimated by applying the following experiments and calculations. In Fig. 3 doping–dedoping curves of PANI electrodes with current density of 1.25 mA cm⁻² for the different doping potential limits are shown.

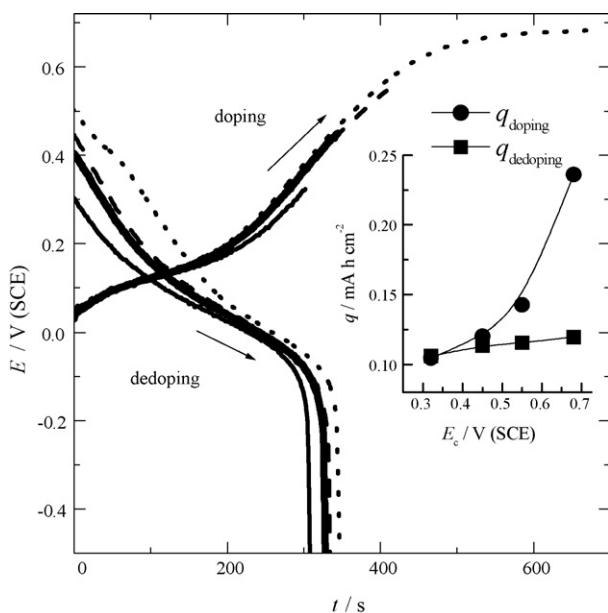


Fig. 3. Doping–dedoping curves of PANI electrodes for the different doping potential limits, with current density of 1.25 mA cm⁻². Insert: dependence of the electrode capacity for different doping potential limits.

Doping of the electrode start at ~ 0.04 V, followed by plateau up to ~ 0.17 V. This plateau can be assigned to the changes of the emeraldine salt doping degree. Above ~ 0.17 V increase of the potential could be attributed to the further emeraldine salt doping, and formation of the degradation products. Plateau at ~ 0.7 V probably corresponds to the redox potential of degradation products and formation of pernigraniline. Open circuit potentials after doping were dependent on the doping potential limits, and varied from 0.3 to 0.5 V, but dedoping curves are very similar. As it can be seen from insert in Fig. 3, obtained dedoping electrode capacity was practically independent on the doping potential limits, and could be assigned only to the dedoping of the emeraldine salt. The maximal reversible electrode capacity of 0.115 mAh cm⁻² was obtained for the doping potential limits of 0.45 V. But, considering the appearance of the degradation products at the potentials above ~ 0.35 V, it should be suggested that PANI electrode in 1.1 M H₂SO₄ has to be doped to approximately 0.35 V.

Since, the dedoping electrode capacity practically corresponds only to the emeraldine salt, the active PANI mass and the current efficiency of the polymerization process of the PANI in 1.1 M H₂SO₄ were estimated by applying the following calculations. The theoretical mass can be calculated assuming 100% current efficiency during polymerization of the aniline, taking into account average molar mass of one monomeric unit in the polymer, and using equation [26,27]:

$$m = \frac{jt(M_m + yM_a)}{(2 + y)F} \quad (4)$$

where m (g) is the mass of the PANI polymerized with current density j (A cm⁻²) over time, t (s) M_m and M_a (g mol⁻¹) are molar mass of aniline monomer (93.13 g mol⁻¹) and inserted, sulfate, anions (96.06 g mol⁻¹), $F = 96,500$ A s mol⁻¹ is Faraday constant, and y is doping degree. Due to the polymerization potentials of ~ 0.56 V, and considering the cyclic voltammogram, see Fig. 1, it should be suggested that after polymerization PANI was mainly in the emeraldine salt state with $y = 0.5$. Using Eq. (4) it could be estimated that theoretical mass of the PANI on graphite electrode was 2.1 mg cm⁻² for applied polymerization current density of 2.5 mA cm⁻² and for polymerization time of 1440 s (1 mAh cm⁻²). Considering the obtained electrode dedoping capacity, $q_{d,el}$, of ~ 0.115 mAh cm⁻², polymerization current density efficiency is given by equation:

$$\eta_{j,pol} = \frac{q_{d,el}(= 0.115 \text{ mA h cm}^{-2})}{y(= 0.5) \times q_{pol}(= 1 \text{ mA h cm}^{-2})} \quad (5)$$

$\eta_{j,pol}$ of $\sim 23\%$ was calculated, which correspond to the active PANI mass of 0.48 mg cm⁻². The relatively low polymerization current density efficiency could be connected with formation of inactive low molecular weight soluble or insoluble polyaniline oligomers. Hence, the obtained dedoping electrode capacity of 0.115 mAh cm⁻² correspond to ~ 240 mAh g⁻¹. The corresponding thickness of PANI electrode, assuming the density of sulfate doped PANI of 1.43 g cm⁻³ [28] was estimated to be ~ 3.4 μ m.

Fig. 4 shows the behavior of PANI electrode during cyclization at a constant current density of 1.25 mA cm⁻². Since the degradation of PANI could occur above ~ 0.35 V, to investigate possibilities of degradation the cycling potentials were limited to 0.45 V for doping and to -0.6 V for dedoping.

From the insert of Fig. 4 can be seen that specific electrode capacity (based on 0.48 mg cm⁻² of PANI) during cyclization has practically constant values of 238 mAh g⁻¹ for doping, and 230 mAh g⁻¹ for dedoping, with Coulombic efficiency of $\sim 97\%$. From these results it could be concluded that in the investigated potential range degradation of PANI does not occur during relatively low number of cycles, but it should be mentioned that during prolonged cyclization some degree of degradation could occur. On the other hand, for the doping potential limits of 0.32 and 0.45 V practi-

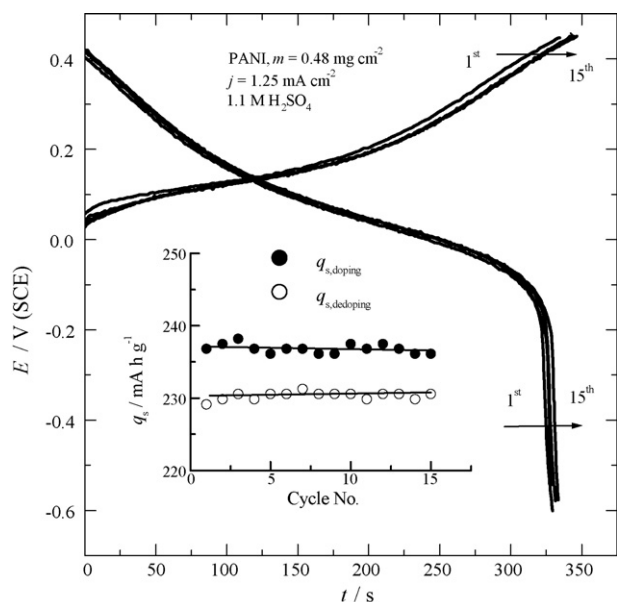


Fig. 4. Doping–dedoping characteristics of the PANI electrode at a constant current density of 1.25 mA cm^{-2} during cyclization. Insert: dependence of the specific electrode capacity on number of cycles.

cally the same dedoping capacity was obtained, see Fig. 3. Hence, it should be again suggested that the optimum potential for charging of the PANI electrode is $\sim 0.35 \text{ V}$.

3.2. Synthesis and characterization of thin film PbO_2 electrode

Fig. 5 shows synthesis and characterization of the thin film PbO_2 electrode. Insert of Fig. 5 shows the galvanostatic template of PbO_2 thin film electrode formation, on the oxide free lead electrode at the current density of 2 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$ and 0.05 M KClO_4 , according to the similar procedure described by Petersson et al. [20,21]. Due to the relatively small electrode capacity of PANI electrode, the applied current density was smaller than originally used by Petersson et al. [20].

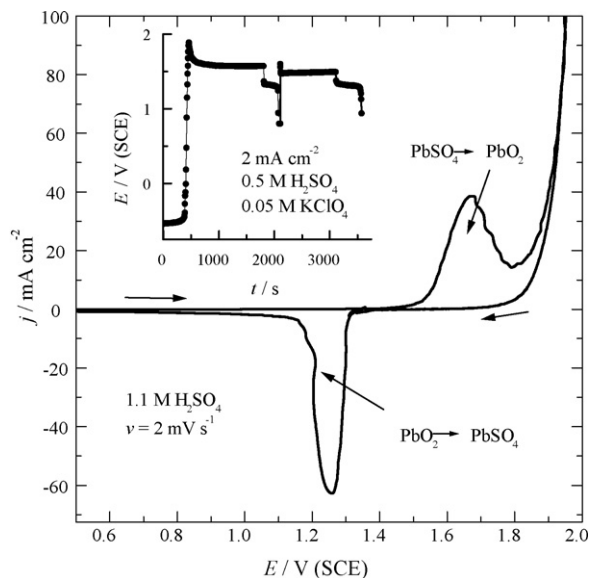


Fig. 5. Cyclic voltammogram of the $\text{PbSO}_4|\text{PbO}_2$ electrode in $1.1 \text{ M H}_2\text{SO}_4$. Insert: PbO_2 synthesis template in $0.5 \text{ M H}_2\text{SO}_4$ and 0.05 M KClO_4 .

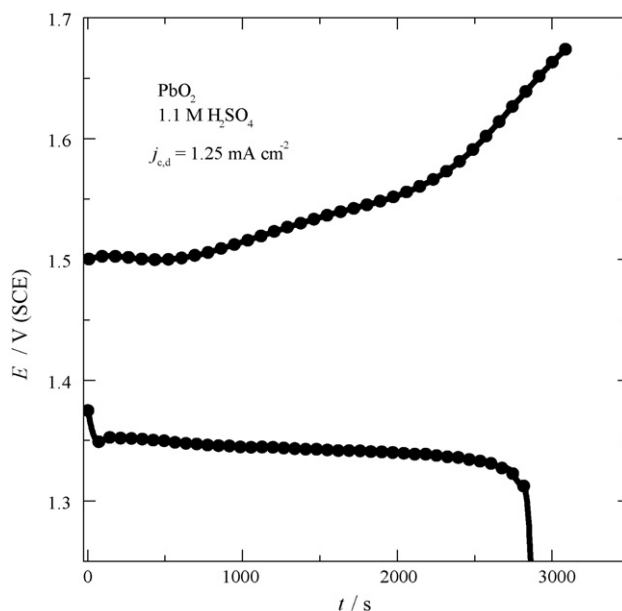


Fig. 6. Typical charge/discharge curves of PbO_2 thin film electrode at a constant current density of 1.25 mA cm^{-2} in $1.1 \text{ M H}_2\text{SO}_4$.

After current was applied, during 400 s potential has the similar value as the open circuit potential, $\sim -0.52 \text{ V}$. This time could be assigned to the induction period, t_{ind} , of the PbSO_4 formation. When most of the lead surface was converted into the PbSO_4 , sharp increase of the potential up to the $\sim 1.85 \text{ V}$ followed by plateau at $\sim 1.55 \text{ V}$ could be connected with the transformation of PbSO_4 to PbO_2 . After 1800 s , electrode was discharged to $\sim 0.75 \text{ V}$ with the same current density, and procedure was reinstated during 1000 s . According to the insert of Fig. 5 the total time which could be connected to the formation of PbO_2 was 2340 s or $\sim 1.3 \text{ mAh cm}^{-2}$. Taking into account Faraday low, and utilization of the formation processes of 100% [20,21], it could be calculated that mass of the PbO_2 was 5.8 mg cm^{-2} , while corresponding PbO_2 thickness was $\sim 6 \mu\text{m}$.

Fig. 5 shows cyclic voltammogram ($v = 2 \text{ mV s}^{-1}$) of $\text{PbSO}_4|\text{PbO}_2$ electrode in the potential range between 0.5 and 1.95 V . Transformation of PbSO_4 to PbO_2 occur in the potential range between 1.4 and 1.8 V through one broad peak, followed by increase of the current density, mostly connected with the oxygen evolution reaction. In cathodic direction, reduction of formed PbO_2 into the PbSO_4 occurs in the potential range between 1.35 and 1.15 V .

A similar result was obtained during the charge/discharge at a constant current density mode, as it can be seen from Fig. 6. Considering the results obtained for PANI electrode, in this mode charge/discharge current density of 1.25 mA cm^{-2} was applied. Charge of the electrode start at $\sim 1.5 \text{ V}$ followed by slow increase of the potential over $\sim 2250 \text{ s}$. After that period of time, faster increase of the potential (for following 860 s) could be connected with oxidation of small amounts of PbSO_4 remains, and oxygen evolution. Discharge of the PbO_2 occur via one well-defined potential plateau of $\sim 1.35 \pm 0.01 \text{ V}$ during $\sim 2850 \text{ s}$. Sharp decrease of the potential after $\sim 2850 \text{ s}$ can be connected with diffusion limitations. The obtained total anodic charge, was 1.08 and cathodic 0.99 mAh cm^{-2} or 186 and 170 mAh g^{-1} , respectively. This result suggests that the current density efficiency of the charge/discharge processes in $1.1 \text{ M H}_2\text{SO}_4$ solution was in the range of $\sim 90\%$, while active mass utilization was $\sim 85\%$.

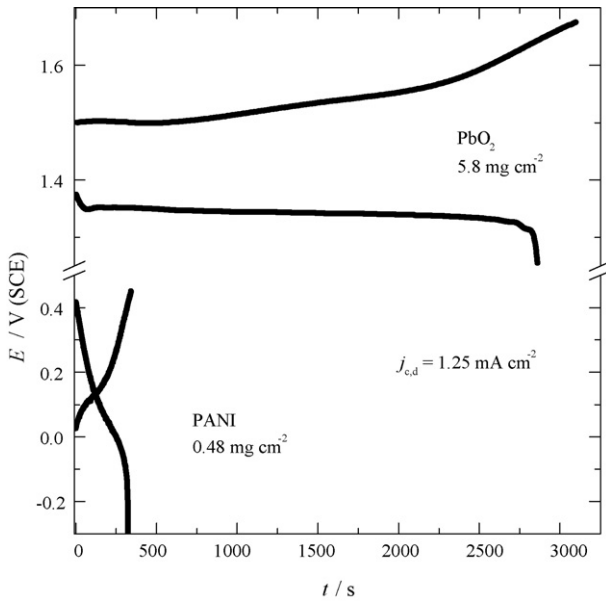


Fig. 7. Charge/discharge curves, extrapolated from Figs. 4 and 6, for simulations of the possible characteristics of PANI|1.1 M H₂SO₄|PbO₂ cell.

3.3. Possible characteristic of the PANI–PbO₂ cell

Considering the obtained results for PANI and PbO₂ electrode, Fig. 7 shows the data taken from Figs. 4 and 6 for simulation of the possible charge/discharge characteristics of PANI|PbO₂ cell in 1.1 M H₂SO₄ for the current density of 1.25 mA cm⁻².

Since, the active mass of PbO₂ electrode was approximately twelve times higher than mass of PANI electrode, 5.8 and 0.48 mg cm⁻², respectively, corresponding charge/discharge times from Fig. 7 was converted into the specific electrode capacity, as shown in Fig. 8.

As it can be seen from Fig. 8 specific electrode capacity of 1 g PbO₂ (shown with full line) was smaller than for 1 g of PANI electrode. Considering the electrode charge balance, it seems that for 1 g of PANI approximately 1.3 g of PbO₂ should be used, as shown with open symbols in Fig. 8.

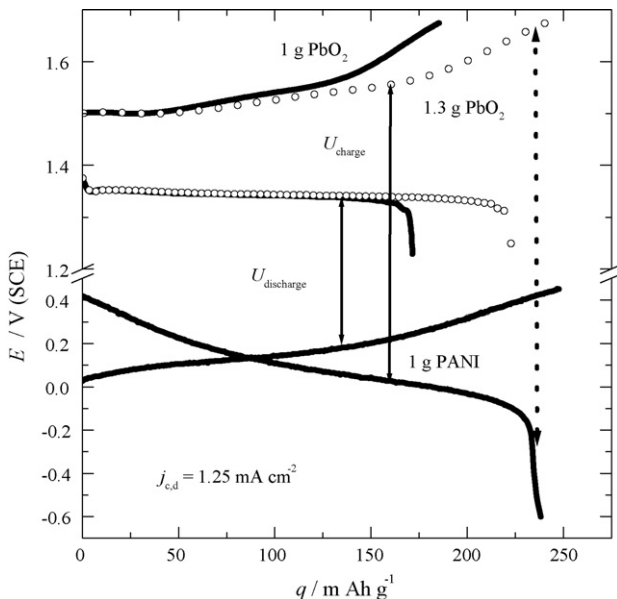


Fig. 8. Dependence of the half cell electrode potentials on specific electrode capacity.

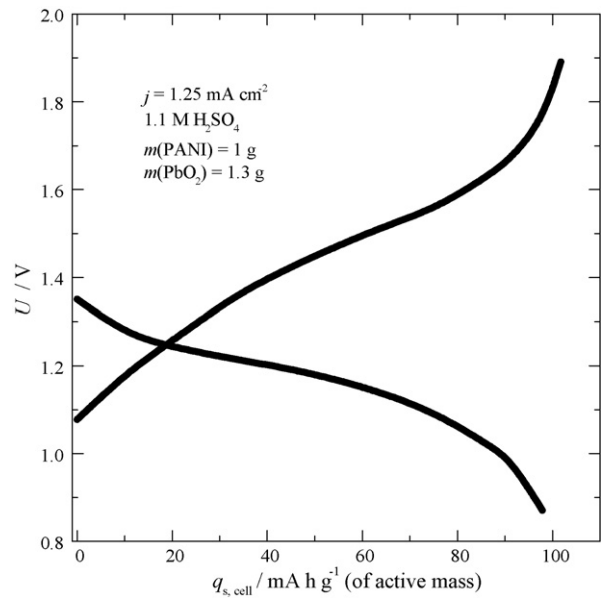


Fig. 9. Simulation of the charge/discharge curves of PANI|1.1 M H₂SO₄|PbO₂ cell, based on 2.3 g of active mass.

Fig. 9 shows the simulation of the possible charge/discharge characteristics during cyclization of PANI|1.1 M H₂SO₄|PbO₂ cell, assuming the total active mass of PANI and PbO₂ per cell of 2.3 g. It was also assumed that for the relatively low current density, voltage loss due to the additional ohmic drops could be neglected.

From Fig. 9 it can be seen that charge of the possible cell will occur in the voltage range between ~1.1 and 1.9 V. In this voltage range most of the charge will be reversibly consumed. Charge of the cell above 2 V can provoke hydrogen and oxygen evolution reaction. After charge, the open circuit voltage will be ~1.35 V which is similar to the classical metal-hydride|NiOOH or Cd|NiOOH cells. Discharge of the cell will occur in the voltage range between 1.35 and ~0.85 V, with the most of the discharge capacity (90 mAh g⁻¹) delivered above 1 V. The average discharge voltage will be ~1.15 V, with the specific energy of ~100 Wh kg⁻¹ which is comparable or higher than for the classical Pb|PbO₂ cell. Potential cell could be occasionally discharged below 0.8 V, which corresponds to PANI doping potential of ~0.4 V. But in that case possibility of PANI degradation could not be excluded.

In comparison with the classical Pb|PbO₂ system according to above presented results and “three E criteria”, PANI|PbO₂ system has some potentially promising characteristics, like: much smaller lead contents and concentration of the electrolyte, comparable or higher specific energy, easier manufacture, and elimination of some problems connected with Pb negative electrode. Disadvantage of such cell in comparison with classical Pb|PbO₂ cell could be mainly connected with much small discharge voltage and small electrode capacity of as synthesized PANI electrode. From that reason, further work is needed in the optimization and characterization of such systems. Optimization has to be performed mainly by the means of PANI synthesis and characterization on high surface area supports, or application of powdered PANI/carbon composites, which should increase the specific active mass of PANI and doping/dedoping current density.

Determination of the cycle life and self-discharge of the cell in real conditions seems to be crucial for further testing and application.

4. Conclusion

Thin film polyaniline and lead dioxide (PbO_2) electrode for the potential application in aqueous based $\text{PANI}|\text{H}_2\text{SO}_4|\text{PbO}_2$ cell, was successfully obtained galvanostatically from sulfuric acid solution. Considering the PANI electrode behavior in 1.1 M H_2SO_4 for different doping potential limits, through different oxidation states, and by comparing the obtained electrode dedoping capacity, it was suggested that maximum doping potential limits was 0.35 V. The obtained specific electrode capacity of PANI electrode was in the range of 240 mAh g^{-1} .

Simulating the charge/discharge characteristic based on the half cell reactions of $\text{PANI}|\text{1.1 M H}_2\text{SO}_4|\text{PbO}_2$ cell, it was estimated that charge of the cell will occur in the voltage range between 1 and 1.9 V, while discharge will occur in the voltage range between 1.35 and ~ 0.8 V, with the most of the discharge capacity delivered above 1 V. Expected specific energy based on the active mass will be in the range of 100 Wh kg^{-1} .

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