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ORIGINAL ARTICLE

Polyaniline–lead sulfate based cell with supercapattery behavior

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Abstract The electrochemically synthesized polyaniline and lead sulfate are investigated as a possible active material of the aqueous based hybrid asymmetric supercapacitors. The electrochemical characteristics of polyaniline (doping-dedoping reactions), as well as electrical characteristics (specific capacitance, capacity, energy, and power) of the $PbSO_4|PANI$ cell, are determined. Based on the estimated specific energy and power, it is suggested that investigated cell could be classified as "supercapattery" type of electrochemical power sources.

1. Introduction

It is generally recognized that different types of the supercapacitor devices could be used as a useful storage system, for the electric energy obtained from the renewable and alternative power sources [1]. The classical electrochemical double layer supercapacitors (EDLC), had the advantages that can deliver high power density (in the ranges of $kW\,kg^{-1}$) and capability (60–120 s typically), excellent reversibility (90–95%), and very long cycle life ($> 10^5$) [2]. Unfortunately, EDLC could store low energy density, typically $3–5\,Wh\,kg^{-1}$ [3]. In order to improve energy density, different pseudocapacitive electrode materials, based for example on transition metal oxides that can store charge by means of redox-based Faradaic reactions, were usually considered [4]. In principle, pseudocapacitive materials can provide the advanced energy density of $\sim 10\,Wh\,kg^{-1}$ [5] than EDLCs, particularly in the systems where numerous discreet oxidation states can be formed during charge/discharge, for examples RuO_2 and MnO_2 [6]. But because the pseudocapacitive electrode materials endure physical changes during the charge/discharge they have relatively poor durability in comparison with the different carbonaceous EDLCs electrode materials. Different asymmetric and hybrid supercapacitor systems were investigated in order to improve electric performances [5,7]. A hybrid device based on a battery type electrode and an electrochemical capacitor electrode defined by Cericola and Kötz [8] as an "internal serial hybrid" (ISH) in principle could combine good characteristics of supercapacitors and battery [9]. Recently, such configuration was named "supercapattery" (from: supercapacitors-batteries) [10,11]. Practically, all the electrode materials of the commercial battery systems can be used for the battery-type electrode in the suitable electrolyte, from lead–acid batteries to metal/air

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systems, but in practice, metallic compounds like SnO_2, MnO_2 and $LiFePO_4$ are usually investigated [10]. One example of such hybrid system based on electrodeposited PbO_2 on graphite in combination with activated carbon negative electrode in 5.3 mol dm^{-3} H_2SO_4 aqueous solutions was recently investigated by Wang et al. [12]. The authors reported a specific capacitance of 63 F g^{-1} in the voltage window from 1.88 to 0.65 V at 5 C rate. The reported specific energy was in the range of 18–27 Wh kg^{-1} with a specific power in the range of 690–150 W kg^{-1}.

Intrinsically conducting polymers (ICPs) represent a distinct group of pseudocapacitive materials that can accumulate energy via both redox and pseudo-capacitive properties [5,13–17]. The ability of ICPs to store charges originates from a doping-dedoping process, and capability to provide the capacitive response through a fast redox reaction of the conjugated areas of the polymer matrix. The most extensively studied ICPs, due to the low cost of the monomer, easy synthesis and environmental friendliness are polyaniline (PANI) and polypyrrole (PPy) with the wide range of the reported specific capacitance in both aqueous and non-aqueous electrolytes [11,16,17]. Recently, we investigated simple supercapattery like cell based on polypyrrole and lead-sulfate in sulfuric acid based electrolyte [18]. The cell shows battery-like behavior at low discharge currents, e.g. < 0.5 A g^{-1}, and supercapacitor-like behavior at a higher discharge currents. Discharge in the specific current range of ~0.1–2.3 A g^{-1} based on the active masses, could provide specific capacity of 90–70 Ah kg^{-1}; specific energy of 60–40 Wh kg^{-1} and specific power in the range of 40–1350 W kg^{-1}, with the specific capacitance of the cell in the range of 300–250 F g^{-1}. This findings inspires us to investigate similar cell, but with polyaniline electrode. The theoretical specific capacitance of PANI is as high as 750 F g^{-1} [17], while the experimentally obtained in the sulfuric acid based electrolytes were reported to be in the range of 200–550 F g^{-1} with potential windows of ~0.8 V [19–21]. The reversible doping-dedoping reaction of the PANI occurred in low pH solutions, $pH < 2$. Under these conditions, due to corrosion instability limited numbers of electrode materials can be used, for example different carbonaceous materials or lead oxide or sulfate. Hence, the aim of this work was to investigate potential characteristics of the hybrid cell with polyaniline as the positive, typical pseudocapacitive materials and lead-lead sulfate as the negative, typical battery electrode material in sulfuric acid based electrolyte.

2. Materials and methods

Polyaniline (PANI) was synthesized from the aniline monomer (ANI) with concentration of 0.25 M in 1 M H_2SO_4 aqueous solution. Prior to use aniline was distilled under reduced pressure. Synthesis was carried out by the galvanostatic method with the current of 15 mA for 1900s (7.9 mAh) onto a plane graphite electrode with dimensions 1.5 cm × 4 cm, $A = 6$ cm^2, platinum gauze counter, and saturated calomel as the reference electrode. Lead sulfate was synthesized by the oxidation of the one side of the thin lead foil with dimensions 1.5 cm × 4 cm, $A = 6$ cm^2, first to spongy lead dioxide, and then by reduction of lead dioxide to lead sulfate. Oxidation was conducted with a current of 9 mA over 450 s (1.125 mAh) in solution contained 1 M H_2SO_4 with the addition of 0.05 M $KClO_4$ as an oxidizing agent [18,22]. Formation of the $Pb|PbSO_4$ electrode was performed in pure 1 M H_2SO_4, by the oxidation of lead sulfate to lead dioxide, and then by reduction of the dioxide to sulfate, and sulfate to pure spongy lead, with a current of 6 mA. Procedure of charge-discharge of lead sulfate to lead and vice versa, was repeated until stable charge-discharge curve was obtained, typically three times. The half-cell reactions, and the determination of the cell performances were conducted in 1 M H_2SO_4.

The electrochemical experiments were conducted using Gamry PC3 potentiostat/galvanostat, in the glass cell with a volume of 100 cm^3, equipped with saturated calomel electrode for potential measurement. The voltage of the cell was recorded using Peak Tech 4390 USB DMM, digital voltmeter connected to PC via USB cable.

For the UV–vis study of as synthesized polyaniline, the product was after synthesis scratched from the graphite electrode surface using a plastic knife, and well ground in an agate mortar. The small amounts of solid product, ~3 mg was added to 10 ml of 1 M H_2SO_4, sonicated in an ultrasound bath for 30 min, and finally, after the precipitation of the larger particles that lasted one hour, 3 ml of the solution was analyzed with an UV–vis LLG uniSPEC 2 spectrometer. For the XRD study of as synthesized $PbSO_4$, the same procedure as for the electrode preparation was applied, only the oxidation was conducted for 2000s, to minimize the influence of pure lead from the electrode bulk. The XRD pattern of the samples was recorded with an Ital Structure APD2000 X-ray diffractometer in a Bragg–Brentano geometry using CuKα radiation and the step-scan mode (range: 15–65° 2θ, step-time: 0.50 s, step-width: 0.02°).

3. Results and discussion

Fig. 1 shows an electrochemical synthesis of polyaniline (PANI) and Pb-$PbSO_4$ active electrode materials on graphite and the thin film lead plane, respectively. Aniline electropolymerization from the aniline monomer (ANI) under galvanostatic conditions occurred at the potentials of ~0.75 V according to the following reaction:

$$n\text{ANI} + n(y/2)\text{SO}_4^{2-} \rightarrow [\text{PANI}^{y+}(\text{SO}_4^{2-})_{y/2}]_n + 2n\text{H}^+ + (2+y)ne \qquad (1)$$

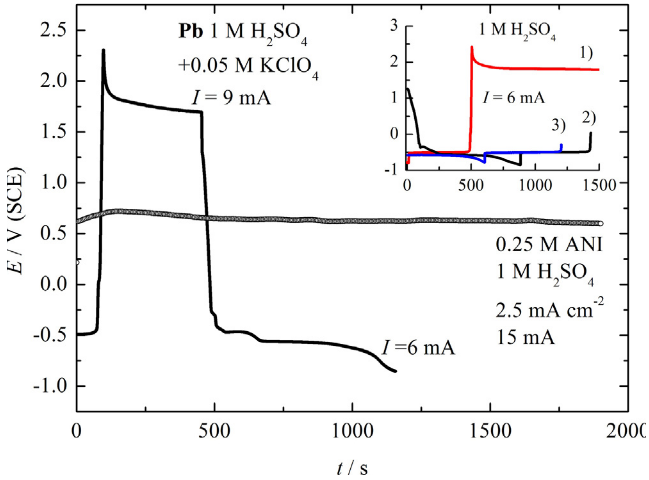

Fig. 1 Galvanostatic formation of the active materials.