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Zinc Polypyrrole-air Sea Water Battery

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An environmentally friendly cell using polypyrrole-air regenerative cathode and zinc as anode, is investigated in the 3.5% sodium chloride solution for the possible applications as the sea water cell. It is shown that cell can deliver constant current in the range of tens of milliamps per gram of polypyrrole, and in the range of hundreds of milliamps under impulse discharge mod, with the cell voltage above 0.8 V, over significant period of time. It is suggested that cell could be considered, at least as a secondary power in a remote sensor buoy system for the monitoring shallow marine environments.

Keywords: Conducting polymers; Air regenerative cathode; Buoy; Metal-air battery

1. INTRODUCTION

In recent years, monitoring of the marine environment became an area of the considerable scientific interest [1]. Shallow marine ecosystems are especially vulnerable, because of the different human actions in the area of the industrial, touristic and municipal expansion. Consequently, pollution monitoring of these ecosystems became the main goal for the scientists concerned in the behavior of the marine environment [1]. It is of great importance to gather information using different sensor devices to ensure successful monitoring of the marine ecosystems [2-4]. A remote sensor buoy system for monitoring shallow marine environments include different electronics components like: sensors devices, radio frequency transmissions module, a power supply with corresponding controlling systems, a set of sensor interfaces, amplification modules, A/D converters, memory for data storage, an electronic timer clock, and finally a microcontrollers (CPU - central processing unit) to integrate the entire process and realized predefined monitoring tasks [5]. Autonomy marine monitoring systems require months of the constant power supply from a battery. In the remote sensor buoy system, the CPU is the main consumer of the power [1]. CPU usually works in an on-off mode with the most of the power, ~80%, consumed during the sleep period. Power consumption depends on the operation mode and range from few microamperes, in a sleep mode, to ~150 mA during the data acquisition, storage and transmission [1]. A power sources usually the Li-polymer battery connected to photovoltaic panel is considered [1, 6, 7]. But such a power supply combination is very heavy, expensive and strongly depends on weather conditions. Namely, Li-polymer battery in combination with photovoltaic panel requires additional electronic components for overcharge and under-discharge limitations, while effective charge with relatively small photocell can be accomplished only during the sunny days. In the occasion of cloudy or foggy days photovoltaic panel should be oversized due small efficiency. For long-lasting power supply, metal-air batteries [8-10], using dissolved oxygen in the sea water as the cathode reactant, should be also considered. The operating voltage of such batteries depends on the metal anode e.g. Mg, Al or Zn, and range from ~1.8 to 1.4 for Mg and some Al alloys with Ga, to below 1 V for pure Al and Zn [11-15]. Conducting polymers, like polyaniline and polypyrrole were used as cathode with zinc anode as potentially promising electrochemical power sources in water based electrolytes [16, 17].

In previous paper it was shown that zinc-polypyrrole cell in 2 M NH_4Cl possess cathode recharge characteristics in the interaction with dissolved molecular oxygen [18]. The recharge was associated with the oxygen reduction reaction onto polypyrrole through two-electron path, accompanied by polypyrrole reoxidation (doping) in the chemical reaction with formed hydrogen peroxide [18]. Hence, the aim of this work was an investigation of the possible characteristics of such cell in the simulated sea water.

2. EXPERIMENTAL

Polypyrrole was synthesized galvanostatically using the current of 48 mA (2 mA cm^{-2}) from electrolyte contained 0.15 M pyrrole (Aldrich p.a., previously distilled under reduced pressure), and 1 M HCl (p.a., Merck) onto both sides of the 3.18 mm thick carbon felt (Alfa Aesar, No: 43199) electrode, with the active area of 24 cm^2, which construction was shown in Fig. 1. The polymerization charge was 30 mAh. During electropolymerization, using saturated calomel electrode as the reference, and two plane-parallel stainless steel plane, 5 cm × 6 cm, as the counter electrodes, electrolyte was mixed with magnetic stirrer at 400 rpm. Two identical pure (>99.9%) zinc plane 4 cm × 6 cm, from the one side isolated by epoxy, were used as the anode.

All experiments were conducted in 3.5% NaCl (p.a. Merck) as the electrolyte. One compartment electrochemical cell made of Plexiglas, with a volume of 500 cm^3 was used. The cathode was inserted between two plane-parallel zinc electrode in a vertical position with an inter distance of 20 mm. Oxygen was supplied from the air using the glass-frit tube as a bubbler, and the air pump with the flow rate of 2 ml s^{-1}, with an oxygen equilibrium concentration of ~0.25 mM at room temperature. For the pulsed charge-discharge experiments combinations of the homemade programmable electronic on-off timer- switcher (1 s to 24 h), and R-substitution box (MA 2200, Iskar, Slovenia), were used.

Experiments were carried out using Gamry PC3 potentiostat/galvanostat, while the cell voltage was collected with digital voltmeter ISO-Tech IDM 73, interfaced to a PC via RS-232.

3. RESULTS AND DISCUSSION

Figure 1 shows galvanostatic electropolymerization of pyrrole onto carbon felt (CF) electrode, which construction was also shown as an image in Fig. 1. Electropolymerization with a current of 48 mA (j = 2 mA cm^{-2}) occurred at potential around 0.6 V. Discharge capacity (Q) can be connected with electropolymerization charge (Q_P) according to [18]:

$$Q = \frac{y}{2+y}Q_p = \frac{y}{2+y}I_p t_p \qquad (1)$$

where y is doping degree, theoretically $y = 0.33$, one chloride anion pre three pyrrole monomer units. Hence, for the electropolymerization charge of 30 mAh, the corresponding maximum available discharge capacity will be 4.25 mAh. The mass of the electropolymerized polypyrrole (PPy) is related with the electropolymerization charge, and can be represented by the following equation [18]:

$$m(\mathrm{PPy}) = \frac{Q_p[M_M - 2M(\mathrm{H}^+) + yM_A]}{(2+y)F} \qquad (2)$$

where, M_M and M_A the molar masses of the monomer unit (M = 67.1 g mol^{-1}) and the chloride anion (M = 35.5 g mol^{-1}). For $y = 0.33$ the mass of the electropolymerized PPy was estimated to ~37 mg.

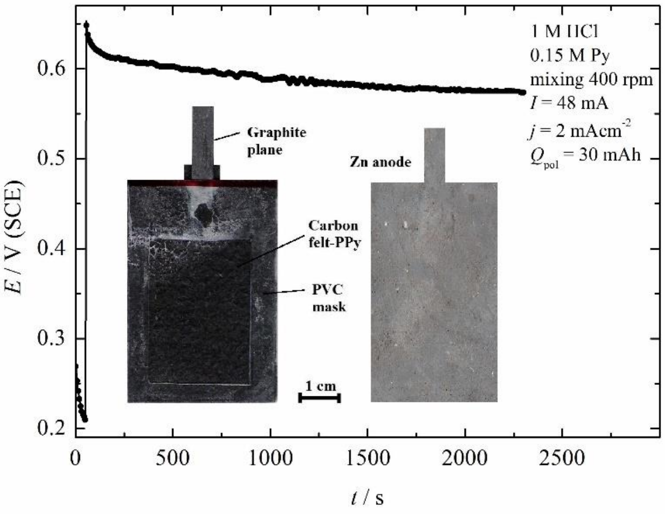

Figure 1. Galvanostatic electropolymerization of pyrrole with current of 48 mA (j = 2 mA cm^{-2}) onto carbon felt electrode, shown in the figure.

The discharge characteristics of the cells with the zinc anode and CF or CF-PPy cathode for different external loads were shown in Fig. 2a. It was obvious that CF-PPy electrode possess much better discharge characteristics than pure CF, because dedoping of the chloride ions and oxygen reduction reactions occurred simultaneously. For example, at 500 Ω the voltage of the Zn|CF cell was

0.6 V (I = 1.2 mA), while for the Zn|CF-PPy cell the voltage was ~1.1 V (I = 2.2 mA). After recording the discharge curves, the external load was switched off and the open circuit voltages over time were recorded, shown in the inset in Fig. 2a. The Zn|CF cell recovered initial voltage of 1.1 V within 30 min. On the other hand, for Zn|CF-PPy much longer time of ~6 h was required for recovery of the open circuit voltage. This can be connected with two reactions occurred at the CF-PPy electrode, similar as in the case of corrosion reaction. First was the oxygen reduction to the peroxide ions as cathodic reaction, and the second was the doping (reoxidation) of the dedoped polypyrrole as anodic reaction, partially assisted with chemical oxidation with released hydrogen peroxide ions. Hence, in the interaction with molecular oxygen, PPy can recover its initial charge. It should be mentioned that small degree of PPy reoxidation by hydrogen peroxide ions can occur also during discharge.

Figure 2b, shows polarization curves of the cells extrapolated from Fig. 2a, as well as dependence of power on applied current. Discharge characteristics of the Zn|CF cell were limited by the low molecular oxygen concentration in the sea water, ranging from 0.35 mM at 0°C to ~0.2 mM at 30°C, and the slow reaction kinetics [20, 21]. Voltage above 0.6 V was obtained only at the low current density below ~0.05 mA cm^{-2}, inset in Fig. 2b. Higher discharge voltage, 0.75 V, for the Zn|CF-PPy cell was obtained even with the current density of ~0.3 mA cm^{-2}, due simultaneous dedoping-doping and oxygen reduction reaction. Obtained maximum power was ~1.5 mW for Zn|CF, and ~5 mW for Zn|CF-PPy cell.

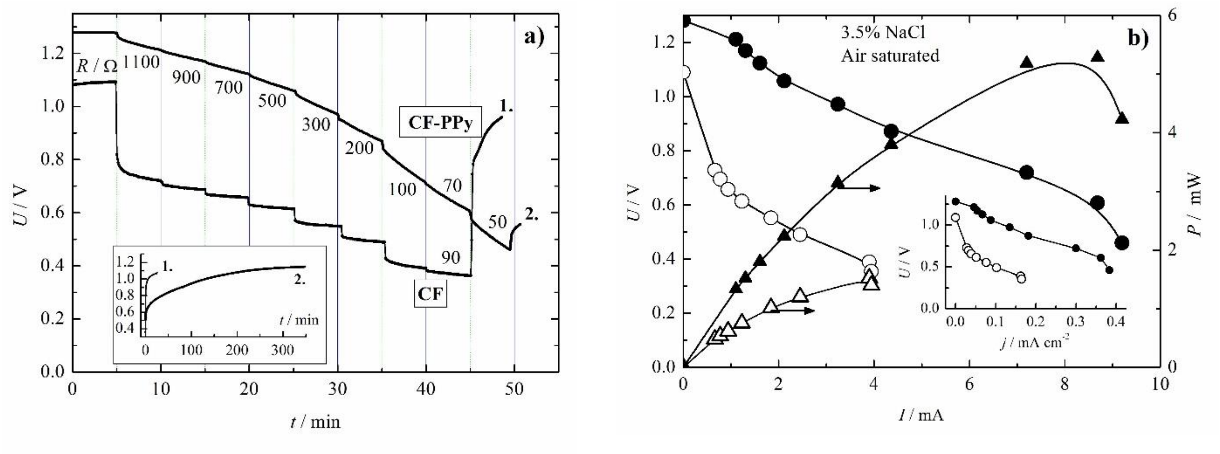

Figure 2. a) The discharge characteristics of the cells with zinc anode and CF or CF-PPy cathode for different external load (marked in the figure) in the non-mixed air saturated 3.5% NaCl. Inset: Dependence of the cell open circuit voltages after discharge over time. b) Polarization curves of the cells extrapolated from Fig. 2a, and dependence of power on applied current (open symbols Zn|CF, full symbols Zn|CF-PPy cell). Inset: polarization curves with respect on the current density.

Reactions which are likely to occur during PPy discharge and reoxidation charge can be anticipated by the following simplified reaction scheme [18]. During discharge at higher voltages, partial dedoping of PPy was the main reaction:

$$[PPy^{y+}(Cl^{-})_{y}]_{n} \rightarrow [PPy^{y+}(Cl^{-})_{y}]_{(n-m)}\text{-}[PPy^{0}]_{m} + myCl^{-} + mye \qquad (3)$$

accompanied by oxygen reduction to the hydrogen peroxide as a parallel reaction, on the quinone-like PPy moieties [18], via followed simplified scheme:

$$[\mathrm{PPy}^{y+}(\mathrm{Cl}^{-})_{y}]_{n}\text{–Py=O} + \mathrm{H_2O} + \mathrm{e} \rightarrow [\mathrm{PPy}^{y+}(\mathrm{Cl}^{-})_{y}]_{n}\text{–Py–OH} + \mathrm{OH}^{-} \qquad (4)$$

$$[\mathrm{PPy}^{y+}(\mathrm{Cl}^{-})_{y}]_{n}\text{–Py–OH} + \mathrm{O_2} \rightarrow [\mathrm{PPy}^{y+}(\mathrm{Cl}^{-})_{y}]_{n}\text{–Py=O} + \mathrm{HO_2^{-}} \qquad (5)$$

The produced hydrogen peroxide ion ($\mathrm{HO_2^{-}}$) was able to chemically reoxidize partially dedoped PPy:

$$[\mathrm{PPy}^{y+}(\mathrm{Cl}^{-})_{y}]_{(n-m)}\text{-}[\mathrm{PPy}^{0}]_{m} + my\mathrm{Cl}^{-} + my\,\mathrm{HO_2^{-}} + my\mathrm{H_2O} \rightarrow [\mathrm{PPy}^{y+}(\mathrm{Cl}^{-})_{y}]_{n} + 3my\mathrm{OH}^{-} \qquad (6)$$

producing better discharge characteristics. At lower voltages, the main reaction was dedoping of the PPy, *via* reaction given by Eq. 3, which gone through diffusion limitations of the counter ions.

The advantage of the Zn|CF-PPy cell can be further used for impulse discharge-reoxidation charge for long lasting cell operation. In order to investigate the potentiality of the cell, the following experiments were conducted, which results were shown in Fig. 3. During constant load (250 Ω) discharge, the cell voltage gradually decreases to 0.6 V over 35 min with average current of 3 mA and capacity of only ~1.7 mAh. Discharge was conducted in air saturated, but not mixed conditions to simulate different oxygen transport, which can occur in shallow sea water. After voltage recovery, the discharge was conducted with 2 min under the load, and 2 min without the load (reoxidation charge). Practically the same discharge capacity was obtained. Increasing the reoxidation charge time to 5 min, the stabilization of the average discharge voltage to ~0.65 V was observed. Introducing the air in the solution (simulating mixing of the sea water under mild, windy conditions), an increase of the cell voltage to ~1 V was observed. This can be explained by different oxygen reduction mechanisms: at low potentials in air saturated solutions, to mainly hydroxyl ions [22] via bridge-type oxygen-carbon adsorption complexes, and mainly to the hydrogen peroxide mechanism under constant oxygen over-pressure and higher potentials [18]. Changing the values of the external load to 100 Ω or 500 Ω under air mixing conditions, the stable average discharge currents of 9 mA and 2.5 mA respectively, were obtained, with the cell voltage above 0.8 V.

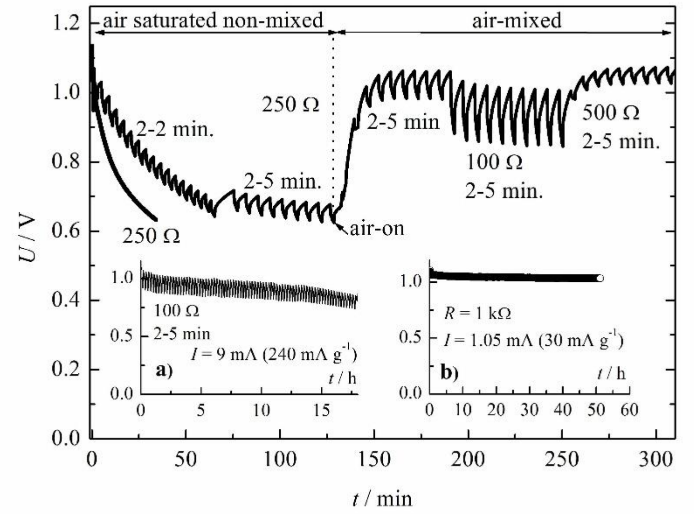

Figure 3. Characteristics of the Zn|CF-PPy cell under continuous and pulsed discharge. a) Constant load (100 Ω) pulsed discharge under air mixing conditions with 2 min. discharge, 5 min recharge period, over time. b) Continuous discharge under air mixing conditions with external load of 1 k Ω over time.

For the pulsed discharge (2 min.) and reoxidation charge (5 min.) under constant load of 100 Ω electrode was discharged over 18 h. with the voltage above 0.8 V, Fig. 3a. The corresponding average discharge current was 9 mA or ~240 mAh g^{-1} of PPy (taking into account that PPy was the main limiting factor of the cell characteristics). The obtained discharge capacity of the cell was 45 mAh (~1.25 Ah g^{-1} of PPy) which ten times exceed available PPy dedoping capacity. On the other hand, during the continuous discharge under 1 kΩ load, the cell voltage was above 1 V over 50 h., Fig. 3b. with corresponding constant current of 1.1 mA (~30 mAh g^{-1} of PPy) and a capacity of 55 mAh (~1.5 Ah g^{-1} of PPy).

According to the results shown in Fig. 3, pulsed discharge-recharge under constant loads and two different on-off conditions were shown in Fig. 4. For the conditions of 10 s discharge under the load of 20 Ω, and reoxidation charge for 60 s, the voltage gradually decreased from 1 V to ~0.8 V over 42 h, while the average current was ~40 mA (~1.1 A g^{-1} of PPy). The delivered capacity was in the range of 4.4 Ah g^{-1} of PPy. For the conditions of 2 min. discharge under the load of 100 Ω, and reoxidation charge for 10 min., the average voltage of 0.9 V did not change significantly over 60 h. The average current was ~9 mA (~240 A g^{-1} of PPy), and the delivered capacity was in the range of 2.6 Ah g^{-1} of PPy.

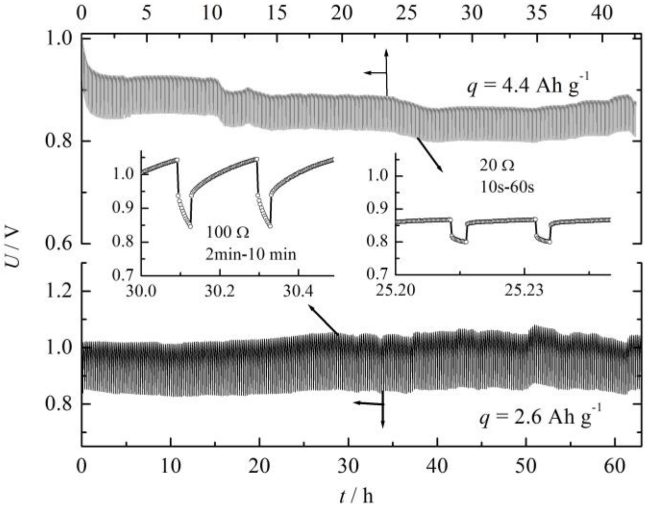

Figure 4. Pulsed discharge-recharge of Zn|CF-PPy cell for external loads of 100 Ω (discharge 2 min, recharge 10 min) and 20 Ω (discharge 10 s, recharge 60 s) in air mixed electrolyte over time.

4. CONCLUSION

The carbon felt electrode modified with polypyrrole possess improved discharge characteristics as a cathode, in comparison with pure carbon felt, in the Zn sea water based cell. Such behavior was explained with ability that polypyrrole can be reoxidized in the interaction with dissolved molecular oxygen. Under the conditions of mild air mixing the cell can operate with constant discharge current of ~30 mA g^{-1} of PPy over at least 50 h, with the voltage above 1 V. Under pulsed discharged-reoxidation charge conditions, the cell can deliver specific currents in the ranges of 0.1 to 1 A g^{-1} of PPy with average discharge voltage above 0.8 V, over significant period of time. Specific discharge capacity obtained in this work for investigated times were in the rages of few Ah g^{-1} of PPy, suggesting that such cell with proper mass of zinc anode could be potentially considered as at least secondary power sources, in combination with smaller Li-polymer battery and photovoltaic panel, in the remote sensor buoy system for monitoring shallow marine environments, for example to power microcontrollers during sleep period. Also it should be pointed out that, proposed cell is an environmentally friendly devices which does not contain toxic organic solvents, or highly reactive lithium compounds. Relatively low average discharge voltage, can be increased by serial connections of three cell (2.5-3 V) with proper elimination of leaking currents, or by using simple miniature micro-power synchronous step-up DC/DC converters like LT3525-3 V; LTC3525-3.3 V; LTC3525-5 V.

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