RECHARGEABLE METAL-AIR BATTERIES WITH CONDUCTIVE POLYMERS CATALYSTS

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Ref. [1] described for the first time the effect of catalytic reduction of air oxygen on a thin polyaniline (PANI) film.

The conducting polymers show a significant non-faradaic component of the electrochemical mechanism. Our investigations of the current-producing mechanism for the PANI electrode have shown that at least within a main working range of potentials ΔEn from 0.30…0.40 to 0.80…0.90V vs. SHE (depending on pH value) the "capacitor" model of ion intercalation/ deintercalations in well conducting emeraldine salt phase is more preferable [2].

The main idea of this R&D is to use *catalytic activity* of PAN-type conducting polymers towards the oxygen reduction during the discharge process of battery side by side with *non-Faradaic process* of anion doping during the charge process for development of rechargeable Air –Met batteries (first of all – Air-Zn battery) with a new low costs composite polymeric catalysts. It gives a possibility to exclude basically the typical side reaction of oxygen evolution during charging of battery, which usually conducts to destruction of catalytic active Air electrode.

The schemes of discharge & charge processes in traditional and such new type of rechargeable batteries can be written as following:

I. Traditional Air-Met Battery (for instance with Carbon Catalysts)

<u>Discharge Process:</u>

$Met^0 - ne \Rightarrow Met^{n+}$ (1)

$O_2 + 4e + 2H_2O \Rightarrow 2OH^-$ (2)

<u>Charge Process:</u>

$Met^{n+} + ne \Rightarrow Met^0$ (3)

$4OH^- - 4e \Rightarrow 2H_2O + O_2$ (4)

<u>*Side reaction:*</u> $C + O_2 \Rightarrow CO_2$ (destruction !!!)

II. Rechargeable Air-Met Battery with PAN-based Catalysts

<u>Discharge Process:</u>

$Met^0 - ne \Rightarrow Met^{n+}$ (1a)

$2O_2 + 4e + 4H^+ \Rightarrow 2H_2O_2$ (electrochemical)

<u>$2H_2O_2 \Rightarrow O_2 + 2H_2O$ (chemical stage)</u>

$O2 + 4e + 4H^+ \Rightarrow 2H_2O$ (2a)

<u>Charge Process:</u>

$Met^{n+} + ne \Rightarrow Met^0$ (3a)

<u>$PAN - ne + nA^- \Rightarrow [PAN^{+n}\bullet nA^-]$ (4a)</u>

(intercalation)

Total: $Met^{n+} + PAN + nA^- \Rightarrow Met^0 + [PAN^{+n}\bullet nA^-]$

For realization of founded catalytic activity of PANI towards the oxygen reduction in real batteries appropriate conditions should be created. First of all, a good air supply to a thin PAN layer should be provided. That is why an optimal carbon substrate with a high conductivity, stability to oxidation, low density and sufficient specific surface is necessary for developing real porous electrode.

It was shown by our experiments and by analysis of the proposed theoretical model for a generalized system "active material - conductive additive" that thermally exfoliated graphite (TEG) can be one of the most effective *support* for the different new and existing active materials of primary and secondary batteries, including "Air (PANI)-Met" system. The reason for such wide application is a following unique complex of TEG properties: low density, relatively high conductivity and stability to electrochemical oxidation during battery serviceability [3].

The composites for such semi-metal batteries contain the chemically or electrochemically synthesized PANI as the first component and (TEG) as the second one. The composition of mixture depends on the further target of composite utilization.

For the development of primary semi-metal batteries the composition contains 30 % of PANI and 70 % of TEG. For the development of rechargeable semi-metal batteries the composition contains 90 % of PANI and 10 % of TEG.

The experimental samples of Air-Zn and Air-Mg batteries with PANI-TEG catalysts were realized in the standard AAA size of MnO_2-Zn primary batteries. The discharge curves for such batteries look enough horizontal (Fig. 1). The discharge curve for Air electrode, which was measured using additional third Ag│AgCl reference electrode, is ideally horizontal since it is determined by the oxygen reduction potential in according medium (Fig. 1, curve 3). The capacities of batteries are limited by the stores of Zn (or Mg) in batteries (Fig. 1, curves 1 and 2). The average weight for the experimental Air-Zn and Air-Mg batteries is 3 g and 2.7 g correspondingly against of 11 g for traditional MnO_2-Zn battery. It is a main reason of sharp increasing the specific energy of Air-Zn (140 W·h/kg) and Air-Mg (200 W·h/kg) batteries against of traditional one (45 W·h/kg).

The specific energy of Air-Zn battery with used slightly acidic electrolyte ($ZnCl_2$ with pH 5) is not very high as compared to ordinary Air-Zn battery with alkaline electrolyte due to the relatively low average discharge voltage (1.0 V during discharge on the resistor of 200 Ohm). Nevertheless, the service life of such systems can be greater than that of ordinary alkaline systems owing to the absence of electrolyte carbonization. For example, some experimental samples of Air-Zn batteries have demonstrated the service life of about 5 years. In addition, the batteries can be rechargeable, the cyclability attained with them ($\geq$ 70 cycles) being limited now only by the properties of used smooth Zn electrode and ordinary separator.

Air-Mg batteries have larger average discharge voltage (1.6 V) and specific energy, but did not have a great service life and abilities for cycling due to the high activity of Mg electrode.

In general, we believe that new types of batteries with composite PANI/TEG catalysts can find own diapason of practical using depending on concrete conditions of application.

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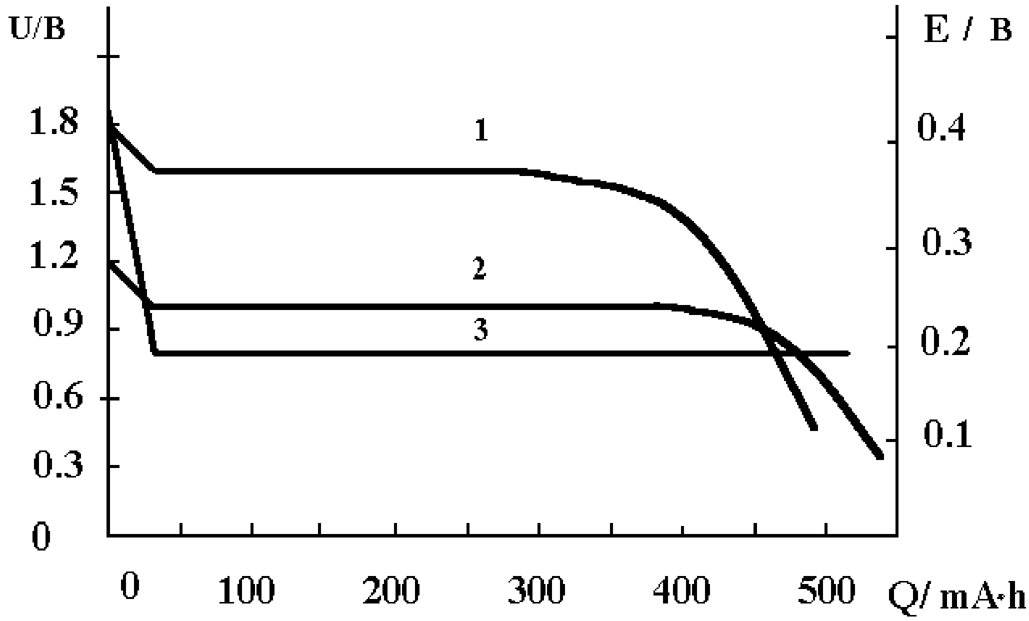

Fig.1. *Discharge curves of AAA size Air/Metal cells (1, 2) with composite PANI catalysts, as well as discharge curve of separate Air electrode (3). Discharge current I =5mA, temperature 18°C.* ***Electrochemical Systems:*** *(PANI) Air | $MgBr_2$ | Mg (1); (PANI) Air | $ZnCl_2$ | Zn (2); (PANI) Air | $ZnCl_2$ | | AgCl | Ag (3).*

Table 2. *Characteristics of cylindrical AA size Air-Metal batteries with PANI/TEG catalysts, as well as MnO_2-Zn battery*

Characteristics of cells	(PAN) O_2|Zn	(PAN) O_2|Mg	MnO_2|Zn
Discharge capacity, mA·h	420	340	380
Specific energy, W·h/kg	140	200	45
Weight of the cells, g	3	2.7	11
Dimensions, cm (H / d)	4.5 / 1.0	4.5 /1.0	4.5/1.0
Open circuit voltage, V	1.2	1.8	1.5
Average discharge voltage, V (at $R_{DISCHARGE}$ = 200 Ohm)	1.0	1.6	1.1-1.3
Short - circuit current, A	1.0	1.2	1.4
Self - discharge, % within a month	1.5-2.0	2.0-4.0	1.0-3.0
Service life, years	~ 5	< 1	< 2
Rechargeability, cycles	≥ 70	--------	------