Fundamentals of Air - Metal batteries with polyaniline-based catalysts

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The chemical energy of atmospheric oxygen can be converted in principle to electrical energy by one of the following main schemes depending on the pH values of the medium and electrode potential:

- in an alkaline medium

$$O_2 + 2\ H_2O + 4e^- = 4\ OH^- \qquad (1)$$

- in an acid and neutral medium

$$O_2 + 4\ H^+ + 4e^- = 2\ H_2O \qquad (2)$$

or

$$O_2 + 2\ H_2O = 2\ H_2O_2 \qquad (3)$$

Each of the variants of carrying out reactions (1)-(3) requires its own catalysts and has its advantages and disadvantages. For example, a fairly wide range of promising catalysts such as:

- metal oxides with the perovskite and pyrochlore structure;
- protective additives based on oxides of variable-valence metals;
- pyropolymers, etc.

appeared in recent years for the development of rechargeable oxigen electrodes in alkaline medium (1). At the same time, a serious problem which limits the service life of real energy-saving devices is the carbonization of alkaline electrolyte.

Passing to acid and neutral media (2,3) makes it possible to avoid the disadvantages caused by electrolyte carbonization. However, the range of possible catalysts becomes in this case much narrower (especially in strong acid media).

Ref. [1] describes the effect of catalytic reduction the air oxygen on a film polyaniline (PAN) electrode. PAN was synthesized by chemical and electrochemical methods. Its composites with different types of graphite and carbon blacks were prepared and selected. The best results in such composites were demonstrated by thermally exfoliated graphite from Superior Graphite Co., Chicago (USA).

The investigations and modeling of the electrochemical behavior of PAN leads to conclusion that in the absence of external oxidizers-reductions within the practically important potential range the electrochemical processes in the polyaniline (PAN) electrodes takes place mainly by the way of charging-discharging the effective capacity of double electric layer [2]. This capacity is abnormally high in the systems under consideration (300...600 F/g) due to formation of double electric layer at a molecular level.

It is possible to explain the phenomenon of catalytic oxygen reduction on PAN using some principles of electronic theory for catalysis formulated by Pisarzhevsky. The relatively high electronic conductivity of PAN connected with the presence of interchange system of poly-π-conjugated bonds. Such system is characterized by a possibility for slight delocalization of electrons under influence of the electric field. A molecule of oxygen can be easy decomposed on two atoms and easy ionized on such conductive poly-π-conjugated bonds. Such bonds structure, electronic conductivity and high effective surface for double layer formation on nanoscale level let us possibility to explain the PAN catalytic activity towards the atmospheric oxygen reduction.

The PAN catalyst can find the practical application for development of real porous electrodes and quite cheap Air/Metal power sources with energy density of about 130-150 Wh/kg for Air/Zn batteries and 200-250 Wh/kg for Air/Mg batteries depending on current densities.

It is possible also to create rechargeable Air/Metal battery using PAN electrodes. During the charging of such battery very fast and reversible process of PAN double electric layer charging takes place instead of common process of oxygen evaluation at positive electrode. It gives a possibility to exclude a positive electrode destruction during the charging. The service life of such battery is limited now by the reversibility of metal electrode and properties of separator.

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References:

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2. V. Barsukov and S. Chivikov, *Electrochimica Acta*, 41, 1773 (1996).