ELECTROCONDUCTIVE POLYMERS & THERMALLY-EXFOLIATED GRAPHITE COMPOSITES AS CATALYSTS FOR OXYGEN REDUCTION

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Introduction

Air (oxygen) electrodes, where molecular oxygen is electrocatalytically reduced, are vital to creation of effective fuel cells and air-metal batteries. Usually noble metals such as platinum play a dominating role as electrocatalysts for the oxygen reduction in the acidic mediums. However, a serious disadvantage of Pt and other noble metals is high cost what is a main limitation for wide commercial application. That is why a search for low-cost electrocatalysts for oxygen reduction (especially from air) has been an important goal of many investigators.

Our team was the first who has founded by accident the effect of catalytic reduction of air (oxygen) on a thin film of polyaniline (PANI) during investigation the mechanism of current-producing process at PANI [1]. The further research of this effect took possibility to clarify the electrochemical mechanism of this side reaction (two-electron reduction of O_2 to H_2O_2 and HO_2^-) [2, 3] and to realize porous gas-diffusion electrodes with such type of catalyst and some carbon (graphite) support [4]. Our recent investigations (in press) have shown the existence of similar reaction practically at all types of conducting polymers / polypyrrole (PPy), polythiophen (PTh), poly (3-methyl) thiophen (PMeT), etc./. PANI and PTh have demonstrate the maximal catalytic activity among the other conducting polymers (CPs).

Results & Discussion

From both theoretical and practical points of view, the questions on the reasons, elementary mechanisms and practical application of this phenomenon seems to be of primary interest.

1. Electrochemical investigations of PANI film

The catalytic activity of the PANI for the oxygen reduction reaction was first characterized by using a film PANI electrode as the working electrode in oxygen- and argon-saturated 1 M HCl solution. Fig.1 shows cyclic voltammograms in these two solutions.

A reduction current is observed with two reduction peaks in the oxygen-saturated electrolyte. In the argon-saturated electrolyte, a single reduction peak at lower current density is observed. From the difference between the reduction currents in the two solutions, the reduction current in the oxygen-saturated solution must be due to catalyzed oxygen reduction reaction.

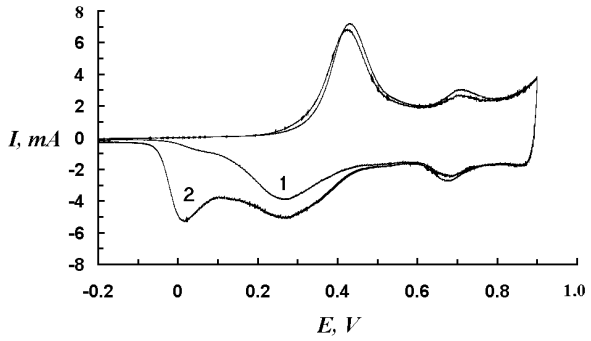

Fig. 1. Cyclic voltamogramms (2 mV/s) of a PANI electrode in argon (1) and oxygen (2) saturated 1 M HCl solution

2. Quantum-chemical modeling

To study the possible reasons and elementary mechanisms of the catalytic activity of CPs, we have modeled the electronic structure of some molecular CPs clusters and its adsorption complexes with oxygen. A MOPAC computer complex and, in particular, the PM3 quantum-chemical program of this complex was used for calculations. The results of calculations have shown that both oxygen atoms form bonds with two more *active carbon atoms* of CP molecular cluster (so-called *"bridge" model* of adsorption). The total energy of system after a che mical adsorption at such *active atoms* is minimal (Fig. 2).

In the CP-O_2^* complex the CP surface is an electron density donor. For example, in the case of PANI the bond orders in adsorbed O_2^* molecules decrease by about 30%, and the bond lengths L increase by about 24%. So, the adsorbed O_2^* molecules have a fairly high degree of activation and can readily interact with the protons in a solution. Further calculations show that in such case H_2O_2 compound forms even inside of adsorption complex. So, it is not

necessary to spent high additional energy for formation of hydrogen peroxide.

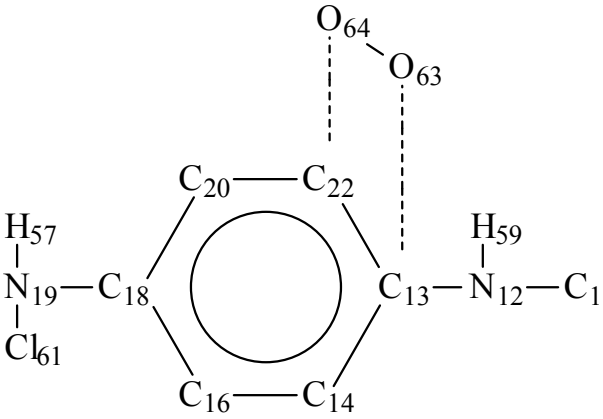

Fig. 2. "Bridge model" of oxygen adsorption on the fragment of PANI structure

Just H_2O_2 is a final product of electrochemical reduction of oxygen that founds a direct confirmation in the experiments.

Thus, quantum-chemical analysis confirms the mechanism of O_2 electroreduction and gives possibility to understand the reasons of catalytic activity of such class new catalysts as PANI and some other CPs.

3. Development of PANI/graphite composites

The next important stage for the development of *PANI/graphite composites* is an investigation of influence of thickness of PANI layer (or more easy controlled parameters like PANI mass and electrochemical capacity) on the local currents of O_2 electroreduction (Table).

Table. *The local currents of O_2 electroreduction at Graphite / PANI electrodes ($S=0.5$ cm^2) with different mass (and electrochemical capacity) of PANI in 1M HCl solution*

PANI mass, mg	PANI capacity mC	I_1, µA	I_2, µA	I_3, µA
0.3	52	13	72	108
0.6	108	27	89	125
0.9	164	31	97	141
1.2	193	33	103	154
1.5	240	37	106	159
2.0	341	39	107	162

The conditions of oxygen supply to the solution: I_1 - with low O_2 content (saturated by N_2); I_2 – with middle O_2 content (saturated by O_2); I_3 – with maximal O_2 content (during O_2 bubbling on the electrode surface)

It is clear that a sharp increase of catalytic activity takes place in relatively thin layer of PANI, which corresponds to the mass of about 0.6...0.9 mg (or Q=108...164 mC) per geometric surface of electrode (0.5 cm^2). Further increasing of PANI thickness (or mass) cannot increase enough the catalytic activity of porous electrode.

Our experiments, as well as analysis of the proposed theoretical model for a generalized system of porous electrode "active material – carbon additive" proved that thermally exfoliated graphite (TEG) can be one of *the most effective conductive additive and structural support* for the different new and existing active materials. The reason for such wide application of TEG is a following unique complex of TEG properties: low density, relatively high conductivity and stability to electrochemical oxidation.

Conclusions

The above phenomena of catalytic activity of CPs toward air (oxygen) reduction have founded a practical application for development of air-metal batteries mockups with low costs PANI/TEG composite catalysts [4]. Specific energy to be attained as primary battery is of about 150 W·h/kg for Air/PANI-Zn and 250 W·h/kg for Air/PANI-Mg batteries. The discharge curves of such batteries is practically horizontal since there are determined by the oxygen reduction potential.

We believe that new type of CPs/TEG composites will find in perspective a practical application also for some types of fuel cells.

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References

1. Chivikov S.V., Barsukov V.Z. and Korneev N.V., Polyaniline activity toward oxygen reduction. In: *Fundamental Problems on Electrocatalysis,* Abstr. III All-Union Conference on Electrocatalysis, Moscow, 1992; p. 155.
2. Barsukov V. and Chivikov S., The "Capacitor" Concept of the Current-Producing Process Mechanism in Polyaniline-Type Conducting Polymers. Electrochimica Acta, 1996; 41: 1773-1779.
3. Barsukov V.Z., et al, On the faradaic and non-faradaic mechanisms of electrochemical processes in conducting polymers and some other reversible systems with solid-phase reagents Electrochim. Acta, 2001; 46(26-27): 4083- 4094.
4. Barsukov V.Z., Khomenko V.G. et al., Physico-chemical fundamentals of development of air-metal batteries with a PANI based catalysts. Electrochemical Power Engineering, 2001; (1-2): 24-30.