

Influence of metal ions on the electrocatalytic oxygen reduction of carbon materials prepared from pyrolyzed polyacrylonitrile

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Abstract

The influence of transition metal ions during a thermal process in which electrocatalysts are made from polyacrylonitrile is discussed. The electrocatalysts were applied on appropriate carbon supports and used for the cathodic oxygen reduction in acid and alkaline electrolytes. Results concerning the electrocatalytic properties of these materials in self-breathing oxygen electrodes as well as the long-term behaviour and the metal dissolution are compared.

Introduction

Nitrogen containing compounds, especially N_4 -chelates, supported at carbon materials have been used as electrocatalysts for the reduction of oxygen in acid electrolytes [1-9]. These materials gain considerably in their electrocatalytic action by a heat treatment in inert gases. During this process the composition and structure of the materials are altered, resulting in the formation of modified materials of higher chemical as well as electrochemical stability. The surface structures which are responsible for this higher electrocatalytic action are still not completely understood but the presence of residual nitrogen atoms attached to carbon surface seems to be of some importance.

Furthermore, the presence of transition metal ions during the heat treatment process and in the formed structure, namely cobalt ions, should influence the properties of the materials formed. A problem in using these catalysts for practical electrodes is the expensive method used to synthesize the N_4 -complexes which afterwards have to be decomposed during heat treatment to form active surface structures.

In some papers [1-5] nitrogen-containing polymers were used instead of the N_4 -chelates and were heat treated in the presence of cobalt salts on appropriate carbon supports. During thermal treatment polymers form modified carbon materials as discussed in ref. 10. The electrocatalytic properties of such materials in alkaline solution were reported by Gupta *et al.* [11, 12]. U Dok Hi *et al.* [8] described the direct dependency

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of the catalytic properties (hydrogen peroxide decomposition in acidic solution) and of the electrocatalytic properties (cathodic reduction of oxygen) in sulfuric acid using polyacrylonitrile-modified carbon heat-treated on the presence of cobalt ions. In this case the electrocatalytic properties of the materials prepared are considerably improved. From that the question arises whether the presence of other metal ions has a similar influence during the heat treatment. Otherwise, the electrocatalytic properties of such materials for the cathodic oxygen reduction in different electrolytes should be compared. In this paper the influence of different transition metal ions on the oxygen reduction at materials prepared by a heat-treatment process using polyacrylonitrile on the performance of oxygen (air) cathodes in alkaline and acidic solution is studied.

Experimental

Metal ions were applied onto a support carbon P33 (properties described in ref. 13) by adding a carbon suspension to the aqueous solution of the salts (sulfates, with the exception of zinc chloride). After drying the carbon at temperatures of about 385 K, polyacrylonitrile (PAN) (chain-polymer prepared by radical polymerization) dissolved in DMF was added. The composition of the product results from addition of 12.3% metal salt and 17.5% PAN to P33. The product was dried at about 420 K and heat-treated at temperatures of 1123 K (with the exception of ZnCl_2 : 600 K) in an argon gas stream for 5 h, similar to the method used in ref. 4. These materials were used as catalysts in double-layer gas-fed electrodes. For the preparation of the electrocatalytic layers the electrocatalyst (PAN-modified and heat-treated carbon) was wet-proofed by adding 15% PTFE from a dispersion (60 wt.% PTFE content). The gas-side layer consists of a hydrophobic gas-permeable layer made of XC-35 (carbon-black with PTFE as wet-proofing and binding agent) [4]. The electrodes were pressed for 1 min at pressures of 22 MPa.

The electrodes were electrochemically characterized in acidic electrolyte (2.25 M H_2SO_4) and alkaline (7 M KOH) electrolytes at 298 K using air and pure oxygen as depolarizing agent at ambient pressure (gas overpressure of only less than 150 Pa). The current density was related to the geometric surface of the self-breathing electrode. Potentials were measured using $\text{Hg}/\text{Hg}_2\text{SO}_4$ (acidic electrolyte) or Hg/HgO (alkaline) reference electrode and are given versus the reversible hydrogen electrode in the same electrolyte (RHE). The heat-treated materials display a sufficient chemical stability and are widely insoluble in the electrolyte. The extraction of the metal ions during the operation time in acidic solution was followed by monitoring the metal content in the acidic electrolyte during the life-time test of the electrode at constant cathodic current density of 5 mA/cm^2 (with air as reactant). The metal content of the electrolyte was determined by atomic absorption spectroscopy. As P33 does not show a significant activity with respect to oxygen reduction in acidic electrolyte, the curve is used as reference in Figs. 1 and 2. The catalyst material prepared with CuSO_4 was not investigated in alkaline electrolyte.

Results and discussion

As shown in Figs. 1 and 2 the materials under investigation catalyze the cathodic reduction of oxygen in acidic electrolyte to a different extent. Best results are obtained using the CoSO_4 -modified carbon material after heat treatment. A somewhat lower

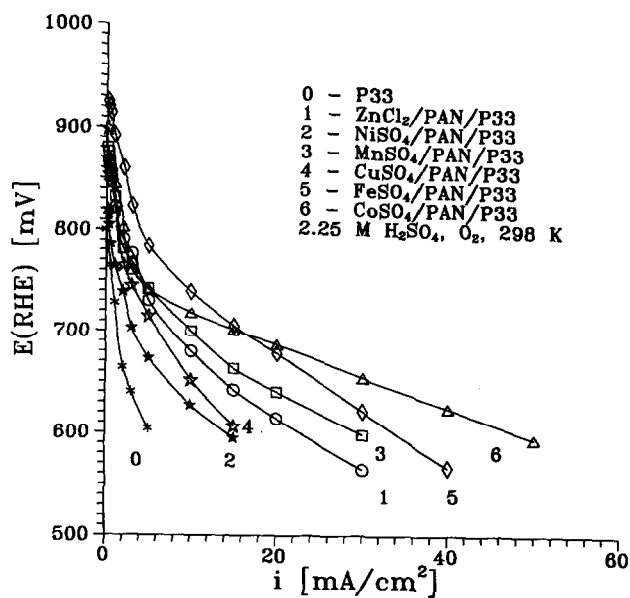


Fig. 1. Polarization curves of oxygen electrodes made from different materials in 2.25 M H₂SO₄ at 298 K.

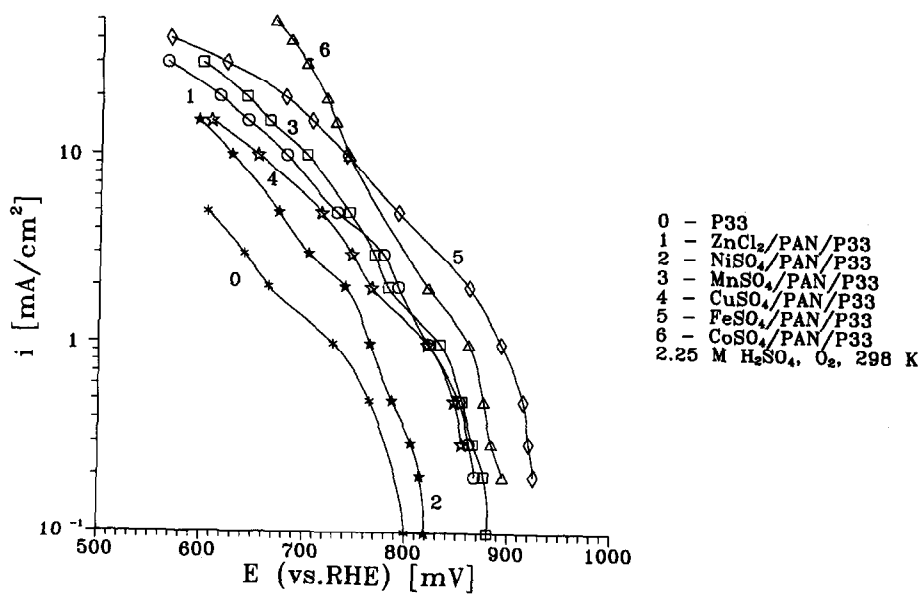


Fig. 2. Logarithmic polarization curves of electrodes from different materials in 2.25 M H₂SO₄ at 298 K.

electrocatalytic action is observed with the iron salt at the same conditions. A remarkable observation is that the rest potential of the iron-containing material is more positive than for the cobalt-containing material. The displayed curves are the initial characteristics of the electrodes. The high rest potential can be explained by the assumption that the iron compound present at the carbon surface is able to easily decompose hydrogen peroxide which may be formed as an intermediate. Thus, the mechanism of the electrode reaction may be shifted to a quasi-4-electron one or the decomposition of hydrogen peroxide becomes so fast that there is no influence of the intermediate on the electrode surface. From the other metal ions investigated only the presence of manganese during the heat treatment improves the electrocatalytic properties of the electrodes in acidic electrolytes whereas zinc, nickel and copper ions do not play any role in the modification of the electrocatalytic surface properties. The reasons may be of a different nature. For instance, the zinc chloride sublimizes even before any metal nitrogen bond may be formed, at temperatures below 670 K.

It has been shown that during operation in acidic electrolytes the iron-based material loses its electrocatalytic action with a significant rate. Thus, after measurement of the $E-i$ characteristics (duration of about 2 h) the iron-based electrode already reveals lower electrocatalytic activity compared to the cobalt-based one. This is illustrated in Fig. 3. In addition to the data represented in Fig. 3 the behaviour of the best electrodes were monitored for more than 2000 h. After 2000 h of utilization potentials of 670 and 580 mV were found for the cobalt-based electrode and the iron-based electrode, respectively. As demonstrated in Fig. 2 the curves do not show a TAFEL behaviour, so they are simultaneously influenced by charge transition and transport processes. This is in agreement with results from *in situ* electrochemical impedance spectroscopy investigations [14]. The long-term experiments show a considerable initial drop of the potential in the case of the iron-based electrode. That is linked to the low stability of this material in acid electrolyte.

In Fig. 4 the remaining metal content in the electrode is given during the lifetime of the electrode. It becomes obvious that in all cases metal is dissolved from the carbon material to a large extent. Also for the most active materials based on cobalt and iron salts the major portion of the metal is extracted from the electrode surface. Thus after 2000 h of utilization the remaining metal contents are only 11%

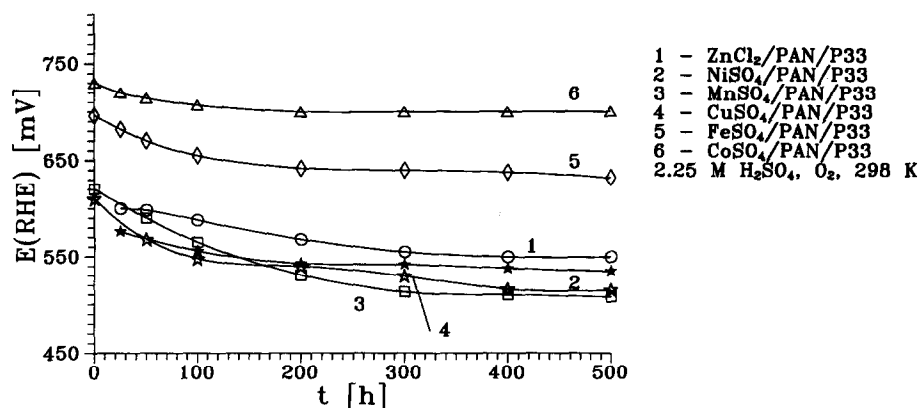


Fig. 3. Potential of oxygen (air) electrodes during long-term experiments using various electrocatalytic materials in acidic electrolyte with constant current density (5 mA/cm^2) at 298 K.

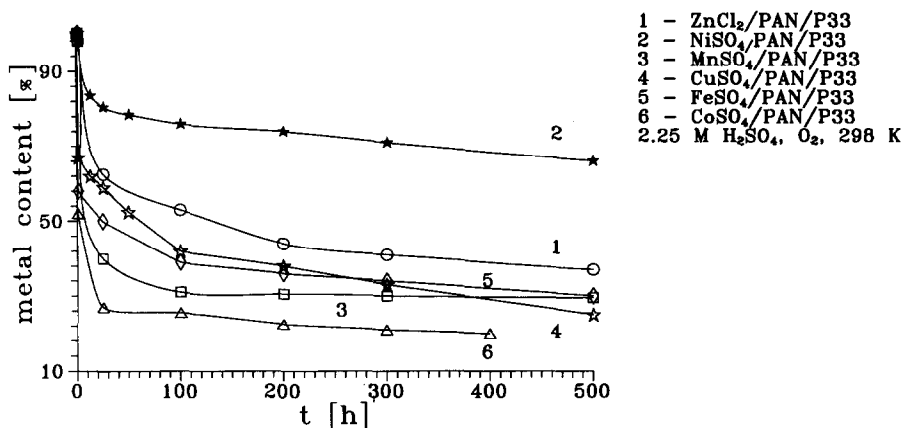


Fig. 4. Remaining metal content in oxygen (air) electrodes during long-term experiments using various electrocatalytic materials in acidic electrolyte with constant current density (5 mA/cm²) at 298 K.

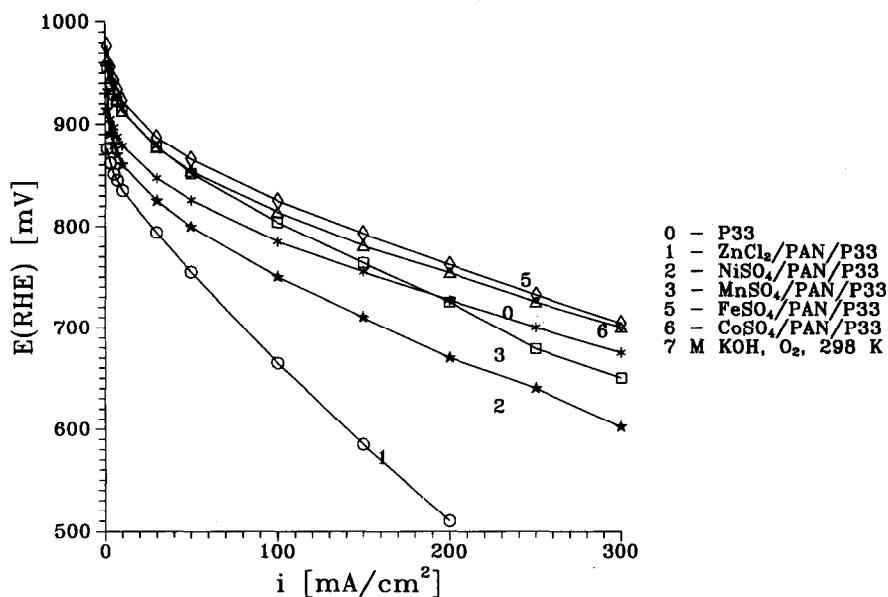


Fig. 5. Polarization curves of oxygen electrodes made from different materials in 7 M KOH at 298 K.

and 20% for cobalt- and iron-based materials, respectively. As a conclusion a direct relation between total metal content and electrocatalytic action cannot be found. But, an explanation for that may be that only a small portion of the metal salt and the polyacrylonitrile may have been converted to form an electrochemically stable and efficient electrocatalyst. This underlines the presence of both metal salt and polyacrylonitrile present during the heat treatment process. The chemical form in which the metal is present at the carbon material may influence the action of the products

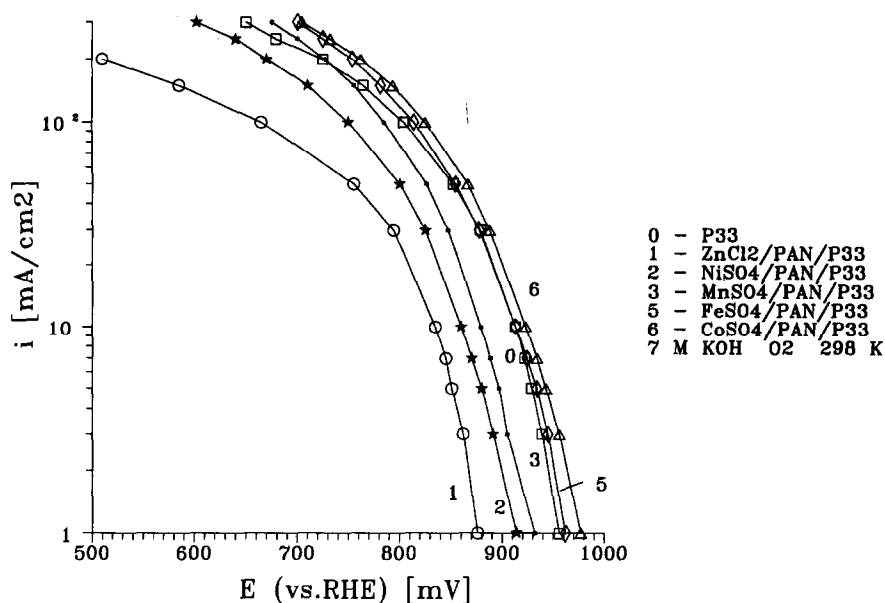


Fig. 6. Logarithmic polarization curves of oxygen electrodes from different materials in 7 M KOH at 298 K.

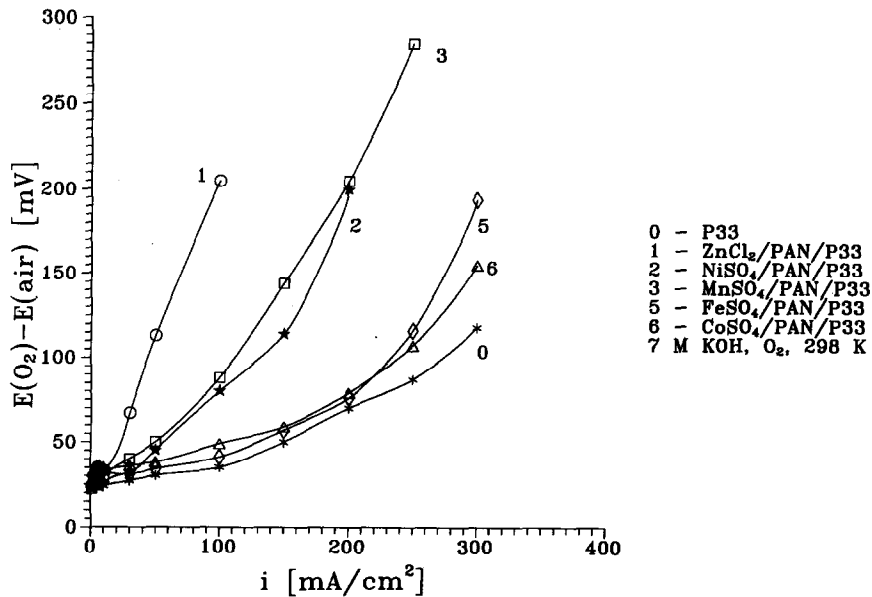


Fig. 7. Breathing curves (difference of potentials using oxygen and air as cathodic reactant) of electrodes made from different materials in 7 M KOH at 298 K.

formed. The reasons for this are the different reaction paths for the annealing process of the metal salts (especially when acetates are used instead of sulfates). In alkaline electrolyte the presence of cobalt salts during the heat treatment of polyacrylonitrile-modified carbons also results in the formation of the most electrocatalytically improved electrodes when compared with the other metal salts (Figs. 5 and 6). But in contradiction to the acidic electrolyte the electrocatalytic effect in comparison to the support carbon is much smaller. For the less active materials even the electrocatalytic action of the support carbon becomes reduced. At low current densities ($< 10 \text{ mA/cm}^2$) the logarithmic polarization curves show linear behaviour with practically similar slopes of 45...50 mV/decade. From that it can be concluded that the mechanism of oxygen reduction is similar for all investigated catalysts. On this base the activity of the electrocatalysts can be compared [15]. The activities decrease in the order of $\text{Co/PAN/P33} \sim \text{Fe/PAN/P33} \sim \text{Mn/PAN/P33} \gg \text{Ni/PAN/P33} > \text{Zn/PAN/P33}$.

The transport hindrances (expressed by the differences of the potentials using oxygen or air as reactants) are shown in Fig. 7. From this the electrocatalysts may be divided into two groups:

- with low transport hindrances (Co/PAN/P33, Fe/PAN/P33)
- with very high transport hindrances (Mn/PAN/P33, Ni/PAN/P33, Zn/PAN/P33).

Other groups have found a considerable gain of electrocatalytic activity in the presence of iron [12]. The reason for the different results may be the different form of the metal salt (acetate where used) and the different electrode structures.

Conclusions

The experimental findings allow the following conclusions to be drawn.

(1) The presence of metal ions during the heat treatment of nitrogen-containing organic compounds on carbon materials is essential to obtain materials of high electrocatalytic action with respect to the cathodic oxygen reduction.

(2) The different metal ions influence the electrocatalytic behaviour of the materials formed to a different extent. In alkaline electrolyte the differences of the electrocatalytic behaviour in comparison to the carbon support is considerably smaller than in acidic electrolytes. This emphasizes that also carbon material itself catalyzes the oxygen reduction in alkaline solution.

(3) As in acidic solution the electrocatalytic action and the stability of the cobalt-based materials differ, it may be assumed that the metal ions play a role in the electrocatalytic reaction and during the heat-treatment process. Thus, only a certain portion of metal ions react to electrocatalytically active *and* chemically stable products. Besides that the cobalt-based material is the best from all the materials investigated.

(4) Even if the electrocatalytic activity of the materials under investigation is lower than that of comparable N_4 -chelates this offers the opportunity for low-cost (starting even from waste materials) electrocatalysts for special applications in electrochemical systems.

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