



Composite electrocatalysts for molecular O₂ reduction in electrochemical power sources

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Composite electrocatalysts for molecular O₂ reduction in alkaline solution with higher activity than a pyrolyzed mixture of cobalt tetramethoxy-phenylporphyrin (CoTMPP) + carbon black were synthesized by pyrolyzing a mixture of CoCO₃ + TMPP + carbon black in an inert atmosphere. Maximum activation was observed at 800 °C. Neither Co₃O₄ + TMPP nor CoCO₃ + TMPP, both mixed with carbon black after pyrolysis, showed better activity than pyrolyzed CoTMPP + carbon black at 900 °C, which points to the presence of carbon as a crucial factor during pyrolysis. Various Co/TMPP mole ratio and CoCO₃/carbon weight ratio were tested. Maximum activity was observed with 1/1 mole ratio and 5% weight ratio, respectively. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

Molecular oxygen reduction in gas diffusion electrodes attracts considerable interest primarily because of its impact on various energy-related fields, such as fuel cells [1,2] and metal-air batteries [3,4]. As an electrocatalyst for this reaction, platinum has traditionally been employed [5,6] but, due to its high cost, less expensive potential alternatives are being actively searched for. Among these, carbon-supported pyrolyzed metal macrocycles exhibit very good activity [7–9] and stability and are currently employed in mechanically recharged metal-air batteries for electrical traction [10].

In pyrolyzed metal macrocycles, the molecular structure of the catalyst is destroyed during the heat treatment so that the metal complex is in fact only a precursor of the actual active material [11,12]. It is thus appealing to try to reproduce these electrocatalysts starting with different precursors of lower cost and easier availability, and to disclose the reasons for their activity so as to be able to improve their performance.

In a previous work [13], we have shown that if cobalt tetramethoxy-phenylporphyrin (CoTMPP) is pyrolyzed at 900 °C with carbon black a very active electrocatalyst results for O₂ reduction in gas diffusion electrodes. Analysis of the composition of the pyrolyzed material showed that some Co₃O₄ was present. For this reason, the activity of Co₃O₄ synthesized from different precursors was investigated. Co₃O₄ from CoCO₃-impregnated carbon black was found to be the most active catalyst. Nevertheless, its

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activity was lower than that of pyrolyzed CoTMPP. Reasons for trying to replace the latter catalyst are two-fold: (i) its precursor is expensive and troublesome to synthesize; (ii) the new synthetic route might lead to more active catalysts. In addition, since the origin of the activity of pyrolyzed CoTMPP is not understood in detail, a study to improve its performance can also throw light onto the factors responsible for its electrocatalytic properties.

Literature works report that the metal needs not be incorporated in the macrocycle before pyrolysis to obtain an active electrocatalyst. Thus, pyrolysis can be applied to a mixture of a metal salt and a macrocycle separately. Research work in this direction has been reported by Gupta et al. [14] and Bouwkamp-Wijnoltz et al. [15].

Since Co_3O_4 was found among the components of the residue of pyrolyzed CoTMPP, a first step was made in this work by producing Co_3O_4 by thermal decomposition of CoCO_3 , then pyrolyzing a mixture of Co_3O_4 + TMPP. Next step was to pyrolyze a mixture of CoCO_3 + TMPP. In both cases, carbon was added after pyrolysis and mixed mechanically. A third step was to pyrolyze a mixture of CoCO_3 + TMPP + carbon. The essential purpose of this work was to investigate a number of experimental variables such as temperature and atmosphere of pyrolysis, as well as the mole ratio between the various components.

2. Experimental

2.1. Chemicals

TMPP and CoCO_3 were purchased from Aldrich. Carbon black (Shawinigan Black AB50, Chevron Co.) was treated at 900°C in N_2 before use.

2.2. Electrocatalysts

Four different preparation routes were tested:

1. CoTMPP + carbon, pyrolysis. Ten weight percent CoTMPP was mixed either mechanically or by impregnation with carbon, then pyrolyzed in N_2 for 1 h at 400, 700, 800, 900°C ('reference' electrocatalyst).
2. CoCO_3 , pyrolysis, mixture with TMPP, pyrolysis mixture with carbon. CoCO_3 was pyrolyzed in air 3 h at 250°C + 3 h at 400°C . Mixed with TMPP, the product was further pyrolyzed in air at 200, 400, 600, 800°C for 1 h. Ten weight percent of the resulting material + 90 wt. % carbon, mechanically mixed.
3. CoCO_3 + TMPP, pyrolysis, mixture with carbon. Ratio 10:1 between TMPP and Co. Pyrolysis at 200, 400, 600, 800°C in air for 1 h. Ten weight percent of resulting electrocatalyst + 90 wt.% carbon, mechanically mixed. Co_3O_4 obtained from CoCO_3 at the same temperatures and mixed with carbon mechanically, was also prepared for the sake of comparison.
4. Precursor of Co (carbonate or nitrate) + TMPP + carbon, pyrolysis at 400, 700, 800, 900°C in N_2 . Amount of Co precursor: 5–10 wt.%. Molar percent of TMPP with respect to Co: 0.5–1.0. Mixed by impregnation.

2.3. Procedure of mixing

- (a) *Mechanical mixture*: The components of the powder were first mixed in an agate mortar, then ultrasonicated in aqueous suspension.
- (b) *Impregnation*: 0.1 mol dm^{-3} Co precursor solution was first mixed with the required amount of TMPP, then slowly with carbon. After 1 h, the temperature was raised to $80\text{--}90^\circ\text{C}$. The powder resulting from the evaporation of the solvent was crushed in an agate mortar, then pyrolyzed as required.

2.4. Preparation of electrodes

The powders prepared as described above were suspended in a mixture of purified water + Nafion and deposited on a Ni support in the form of a $10 \text{ mm} \times 10 \text{ mm} \times 0.2 \text{ mm}$ platelet up to a loading of ca. 1.2 mg. The deposited material was cured at 80°C for 1 h.

2.5. Solution

Electrodes were characterized and tested in N_2 or O_2 saturated 1 mol dm^{-3} KOH aqueous solutions prepared volumetrically with Millipore MilliQ water and Aldrich ACS grade KOH.

2.6. Reference electrode

Potentials were measured and are reported against a saturated calomel electrode (SCE).

2.7. Techniques

Electrodes were characterized by means of cyclic voltammetry at 20 mV s^{-1} in the potential range -0.5 to 0.3 V (SCE) in the presence and in the absence of bubbling O_2 . They were also tested by means of steady-state potentiostatic curves between -0.1 and 0.4 V (SCE) in O_2 saturated KOH solution.

2.8. Instrumentation

Model 273A EG&G Potentiostat–galvanostat controlled by a PC.

3. Results and discussion

Since static electrodes were used, activity is subject to mass transfer limitations at high reaction rate (current densities). Thus, the analysis is confined to the low overpotential region. However, it is precisely in this region that comparison between different electrocatalysts is most significant since the electrode behavior depends more on the intrinsic activity of the catalyst.

3.1. Pyrolyzed CoTMPP + C

It constitutes the electrode material to be improved or reproduced. Therefore, results related to this system are reported first as a reference. The composition corresponds to that actually used in mechanically rechargeable Zn-air batteries [10].

Fig. 1 shows steady-state current density (j)–potential (E) curves for various temperature of pyrolysis. An electrode prepared using the ‘reference’ electrocatalyst (900°C) is also included. Electrodes in the range 700 – 900°C exhibit almost the same activity, although with slight increase as the temperature is increased. The method of mixing does not appear to produce significant effects.

An interesting aspect requiring further specific studies is the apparent high activity of the electrode pyrolyzed at 400°C . Reasons for that have not been investigated in detail because of the poor stability of such material. Higher temperatures of pyrolysis appear to stabilize electrocatalysts.

3.2. Pyrolyzed TMPP + Co_3O_4

Fig. 2 shows, in a semilogarithmic E – j diagram (Tafel plot), that this material is systematically less active than pyrolyzed CoTMPP, the activity decreasing with increasing temperature of pyrolysis. The effect of temperature is probably related to the decreasing

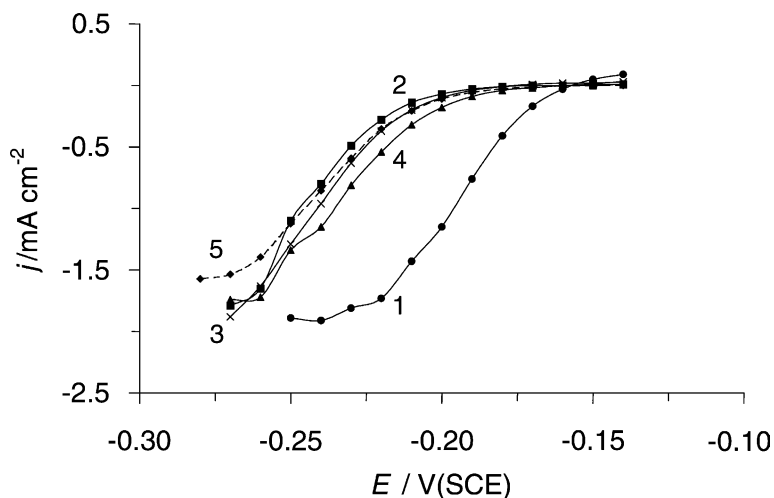


Fig. 1. Current–potential curves of pyrolyzed CoTMPP + 90 wt.% carbon (mechanical mixture) for O_2 reduction in 1 mol dm^{-3} KOH solution. Temperature of calcination: (1) 400 ; (2) 700 ; (3) 800 ; (4) 900°C ; (5) ‘reference’ electrocatalyst.

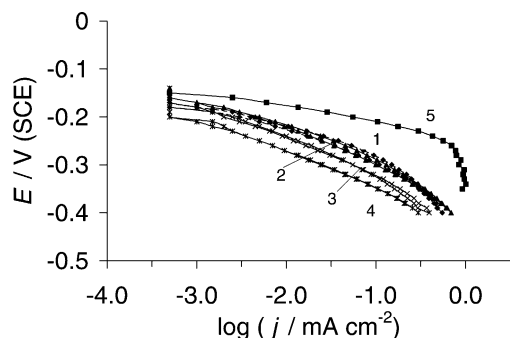


Fig. 2. Current–potential curves of pyrolyzed Co_3O_4 (preformed) + TMPP (1/1) mechanically mixed with carbon. Temperature of pyrolysis: (1) 200; (2) 400; (3) 600; (4) 800 °C; (5) ‘reference’ electrocatalyst (cf. Fig. 1).

surface area of Co_3O_4 with increasing crystallization and sintering. These results suggest that Co_3O_4 does not increase its activity in the presence of TMPP, which indicates that under similar conditions Co- and N-containing molecular moieties do not interact to produce synergetic effects.

3.3. Pyrolyzed CoCO_3 + TMPP

Fig. 3 shows that the simultaneous decomposition of the Co precursor and the macrocycle does not produce active electrocatalysts. Again the activity decreases with increasing temperature of calcination. The higher

activity at 200 °C is puzzling since at this temperature the macrocycle is probably not pyrolyzed. Thus, the apparent activity may be also related to competing parallel processes.

The view is corroborated by the results obtained with pyrolyzed CoCO_3 only. Fig. 4 shows that the voltammetric charge (obtained by integration of voltammetric curves in the absence of O_2 , cf. Section 2) of pyrolyzed CoCO_3 increases with decreasing temperature as observed elsewhere by one of us [16], while the presence of TMPP keeps the voltammetric charge almost constant with the calcination temperature. Nevertheless, the apparent activity is much higher at 200 °C for the samples with TMPP than for that with only CoCO_3 . Thus, between 400 and 800 °C surface area effects related to the decreasing crystallite size of Co_3O_4 are presumably operating, while at $t < 400$ °C, the situation is probably complicated by side effects related to incomplete thermal decomposition of the precursors, especially TMPP.

Fig. 5 summarizes the results for the systems discussed above. It is evident that, apart from 200 °C where problems of decomposition probably exist, the difference between the various methods of electrocatalyst preparation is not significant at the other temperatures. This suggests that while Co_3O_4 is itself active [13], the interaction between Co and N moieties is not the primary source of electrocatalytic activity. The simultaneous presence of carbon during pyrolysis seems to be essential.

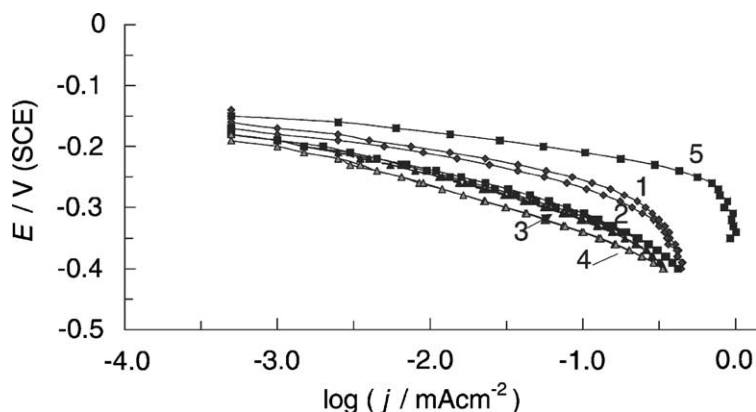


Fig. 3. Current–potential curves of pyrolyzed CoCO_3 + TMPP (1/1) mechanically mixed with carbon. Temperature of pyrolysis: (1) 200; (2) 400; (3) 600; (4) 800 °C; (5) ‘reference’ electrocatalyst.

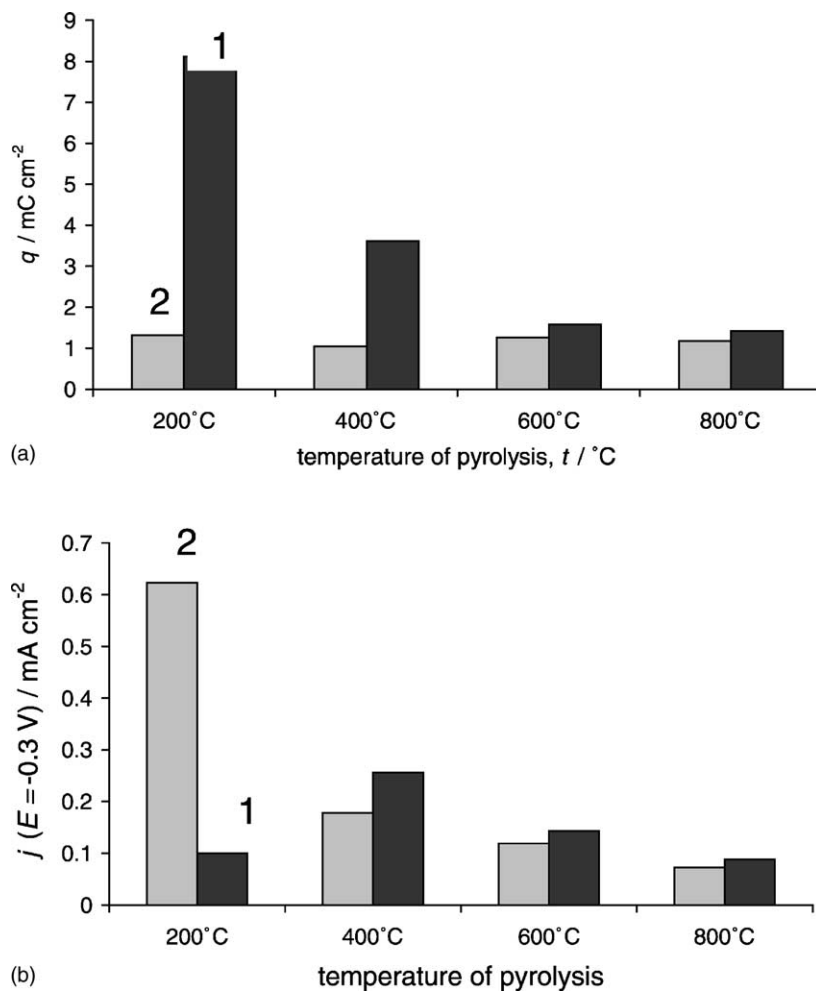


Fig. 4. (a) Voltammetric charge against pyrolysis temperature. (1) CoCO_3 (+ carbon); (2) CoCO_3 + TMPP (+ carbon). (b) Current for O_2 reduction at constant potential against pyrolysis temperature. (1) CoCO_3 (+ carbon); (2) CoCO_3 + TMPP (+ carbon).

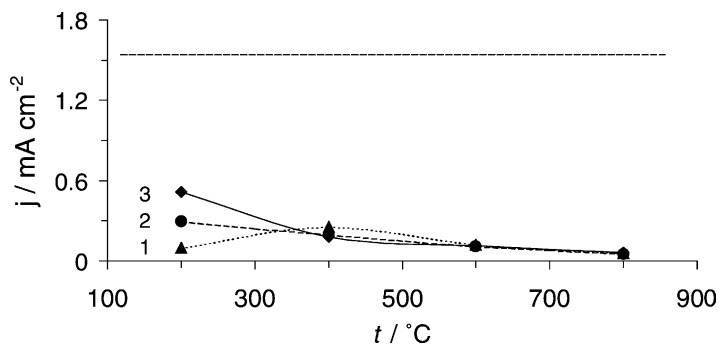


Fig. 5. Current for O_2 reduction at $E = -0.3 \text{ V(SCE)}$ against calcination temperature. (1) Co_3O_4 ; (2) Co_3O_4 + TMPP; (3) CoCO_3 + TMPP. (---) 'reference' electrocatalyst.

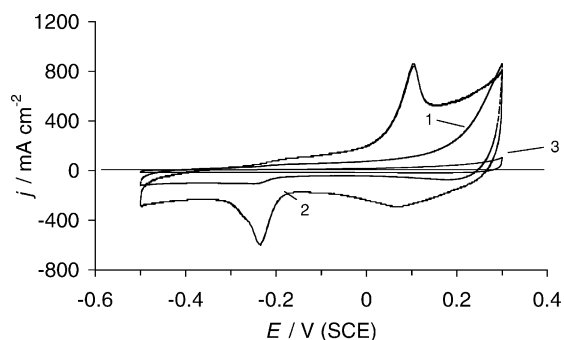


Fig. 6. Cyclic voltammetry at 20 mV s^{-1} in deaerated 1 mol dm^{-3} KOH solution. $\text{CoCO}_3 + \text{TMPP}$ pyrolyzed at (1) 400°C ; (2) 800°C ; (3) 'reference' electrocatalyst.

3.4. Pyrolyzed $\text{CoCO}_3 + \text{TMPP} + \text{carbon}$

The simultaneous pyrolysis of the three components produces a dramatic increment in the activity of the resulting electrocatalyst. At the same time, the CV curve changes shape drastically. As Fig. 6 shows, the voltammetric charge increases with respect to the 'reference' electrocatalyst. In particular, a cathodic and an anodic peak appear whose height increases up to 800°C to decrease again at higher temperatures. CV curves in the presence of O_2 shows that O_2 reduction takes place in the same potential range where the cathodic peak

develops in Fig. 6. Thus, the cathodic peak might be due to a surface redox transition responsible for the activity in O_2 reduction [17]. The anodic peak is presumably related to reoxidation of the surface active sites. Apparently this surface redox couple develops optimally at 800°C .

Fig. 7 shows steady-state polarization curves for O_2 reduction. It is evident that the simultaneous decomposition of the separate precursors enhances the activity of the catalyst at all calcination temperatures. Experiments at different temperatures have shown that the activity goes through a maximum at 800°C , in parallel with the surface charge. If the activity ratio is compared with the charge ratio with respect to the 'reference' electrocatalyst, the enhancement of the activity can be associated with an increase in the surface concentration of active sites.

While in Fig. 7, the curves move horizontally, which might indicate (although not necessarily) that the nature of the active sites is the same, the situation differs from that in Fig. 3 where a change in Tafel slope is visible, i.e. a change in mechanism, which understands a different nature of the active sites. Therefore, the presence of carbon might be responsible for a partial reduction of Co_3O_4 , which makes some interaction between Co ions and nitrogen moieties possible.

Experiments with a different CoCO_3 to carbon ratio showed that increasing the content of the Co precursor

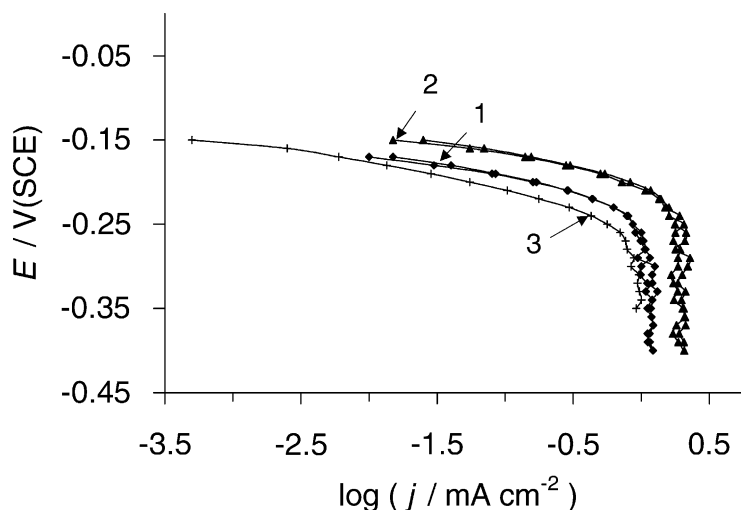


Fig. 7. Current-potential curves in O_2 saturated 1 mol dm^{-3} KOH solution. $\text{CoCO}_3 + \text{TMPP}$ pyrolyzed at: (1) 400°C ; (2) 800°C ; (3) 'reference' electrocatalyst.

from 5 to 10 wt.% decreases the activity of the electrode. Also, a change from a 1:1 mole ratio between Co and TMPP to 4:3 and 2:1 decreases the activity, although the voltammetric charge is either comparable or higher. This indicates that the Co sites, which are not bonded to nitrogen moieties, contribute to the voltammetric charge but not to the activity. It is interesting that in any case the activity goes through a maximum at 800 °C.

If CoCO_3 is replaced by $\text{Co}(\text{NO}_3)_2$, which is a more popular precursor for Co_3O_4 formation, higher activity is observed at 400 °C, but lower at 600 °C. At higher temperatures, no residue is left by the pyrolysis. Reasons are clear: the decomposition of the nitrate produces an oxidant atmosphere due to nitrogen oxides, so that carbon is burned to CO and CO_2 if the decomposition temperature is too high.

3.5. Global picture

Experiments showed the repeatability of the picture illustrated above beyond any doubts. In particular, the level of activity of electrocatalysts based on pyrolyzed CoTMPP was confirmed in two different laboratories [10,13].

A global picture of the situation is shown in Fig. 8, where the current density at constant potential is plotted against the calcination temperature for the various mixtures of precursors. It is evident that only the equimolar mixtures of TMPP + CoCO_3 (+ carbon) show improved activity with respect to the 'reference' catalyst, with a maximum around 800 °C. Next, but

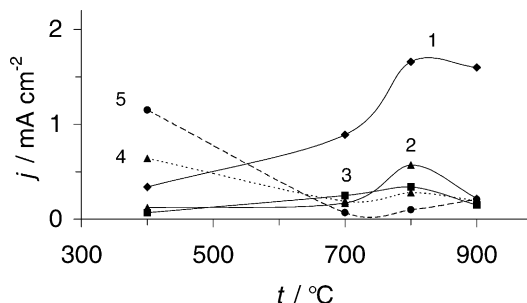


Fig. 8. Electrocatalytic activity at -0.2 V(SCE) for O_2 reduction of pyrolyzed CoCO_3 + TMPP + carbon in 1 mol dm^{-3} KOH solution against pyrolysis temperature. CoCO_3 /TMPP mole ratio: (1) 1/1; (2) 2/1; (3) 4/3. Co/carbon ratio: (1–3) 5 wt.% CoCO_3 ; (4 and 5) 10 wt.% CoCO_3 ; (5) 'reference' electrocatalyst.

with a significantly lower improvement restricted to 800 °C, mixtures with $\text{TMPP}/\text{CoCO}_3 = 0.5 \text{ mol.}\%$. It is interesting that in all cases of mixtures of precursors, 800 °C appears to be an optimal calcination temperature.

4. Conclusions

This work has shown that pyrolyzed CoTMPP + carbon can be replaced with pyrolyzed CoCO_3 + TMPP + carbon. The replacement results in an appreciable increase in activity for a calcination temperature of 800 °C in inert atmosphere. These results confirm previous observations suggesting that the structure of the metal macrocycle is not the factor responsible for the electrocatalytic activity of the resulting material [11,12]. The origin of the activity is the simultaneous presence of metal precursor, active carbon and a source of nitrogen. This has long been known in the case of electrocatalysts for O_2 reduction in acid media [14,15]. The results reported in this work refer for the first time to alkaline solutions. Further work will be required to optimize both the metal precursor and the source of nitrogen.

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References

- [1] K. Kinoshita, *Electrochemical Oxygen Technology*, Wiley, New York, 1992.
- [2] S. Gottesfeld, in: R. Alkire, H. Gerischer, D. Kolb, C.W. Tobias (Eds.), *Advances in Electrochemical Science and Engineering*, vol. 5, VCH, Weinheim, Germany, 1997, p. 195.
- [3] M.I. Bazanov, et al., *Russ. J. Electrochem.* 32 (1996) 1037.
- [4] F.R. McLarnon, E.J. Cairns, *J. Electrochem. Soc.* 138 (1991) 645.
- [5] E. Yeager, *Electrochim. Acta* 29 (1984) 1527.
- [6] A.J. Appleby, *J. Electroanal. Chem.* 357 (1993) 117.
- [7] I. Iliev, S. Gamburzev, Kaisheva, *J. Power Sources* 17 (1986) 345.
- [8] M. Tsionsky, O. Lev, *J. Electrochem. Soc.* 142 (1995) 2132.

- [9] A. Biloul, P. Gouérec, M. Savy, G. Scarbeck, S. Besse, J. Riga, *J. Appl. Electrochem.* 26 (1996) 1139.
- [10] M. Maja, C. Orecchia, M. Strano, P. Tosco, M. Vanni, *Electrochim. Acta* 46 (2000) 423.
- [11] K. Wiesener, *Elektrokhimiya* 18 (1982) 758.
- [12] P. Gouérec, M. Savy, *Electrochim. Acta* 44 (1999) 2653.
- [13] C. Mocchi, A.C. Tavares, S. Trasatti, P. Tosco, M. Manzoli, F. Boccuzzi, in: E.W. Brooman, C.M. Doyle, C. Cominellis, J. Winnick (Eds.), *Energy and Electrochemical Processes for a Cleaner Environment*, vols. 2001–2023, The Electrochemical Society, Pennington, NJ, 2001, p. 362.
- [14] S. Gupta, D. Tryk, I. Bae, W. Aldred, E. Yeager, *J. Appl. Electrochem.* 19 (1989) 19.
- [15] A.L. Bouwkamp-Wijnoltz, W. Visscher, J.A.R. van Veen, S.C. Tang, *Electrochim. Acta* 45 (1999) 379.
- [16] S. Ardizzone, G. Spinolo, S. Trasatti, *Electrochim. Acta* 40 (1995) 2683.
- [17] A.C.C. Tseung, S. Jasem, *Electrochim. Acta* 22 (1977) 31.