Pyrolyzed Co-phtalocyanine as a catalyst for the oxidation of sulphur dioxide

K. Petrov[*], Iv. Nikolov, T. Vitanov, D. Uzun, V. Ognjanov[1]

Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences
(IEES-BAS), G. Bonchev Str., Bl 10, 1113 Sofia Bulgaria;
[1]Institute of Organic Chemistry, Bulgarian Academy of Sciences
G. Bonchev Str., Bl 9, 1113 Sofia Bulgaria

The catalytic activity of pyrolyzed Co-phtalocyanine, deposited onto active carbon "Norit-NK" for oxydation of sulphur dioxide in sulphuric acid media was investigated. The optimum phtalocyanine content and the best pyrolysis temperature of this catalyst were determined. It was shown that gas diffusion electrodes (GDE), catalyzed with Co-Phtalocyanine, pyrolyzed at 700°C ensure 500 hours operation at current density of 60 mA.cm^{-2} with increase of polarization approximately of 50 mV.

Keywords: sulphur dioxide, pyrolyzed Co-phtalocyanine

INTRODUCTION

Sulphur dioxide oxidation has been used for production of hydrogen and sulphuric acid under very favourable energy saving conditions [1]. An original approach was proposed in our laboratory (IEES) [2]. This approach is based on use of GDE which utilize gases containing SO_2. In such a way the production of hydrogen can be combined with purification of waste gases form SO_2. GDE developed in IEES are catalyzed with pyrolyzed metal chelate complexes: dibenzo-cobalt-tetra-azaanulene (CoTAA), cobalt tetra-methoxy-phenyl-porfirine (CoTMPP), and modified active carbon (MC) [3, 4]. Although the initial characteristics were quite promising, the long-term tests of electrodes modified with the above catalysts, revealed that their activity decreased rapidly. On the other hand, the synthesis of these chelate complexes proved to be rather expensive and labour-consuming. These shortcomings stimulated the research to find a catalyst which is more stable in sulphuric acid solutions, easily available, and cost-efficient.

Literature data provide evidence that the metal complexes of phtalocyanines and their pyrolyzed products display catalytic activity toward several electrochemical processes, including the oxidation of SO_2 [5-11]. According to Bagotski et al [6], the activity of metal chelate complexes and their pyrolysis products at 800°C with respect to this reaction diminish in the following order: CoTAA >> CoTMPP > CoTPP > CoPc (Co-phtalocyanine).

Probably this is the reason why the last compound in this row, as well as its pyrolytic derivatives, has attracted less attention in the investigations in this field. Since CoPc is more available and less expensive [12, 13] than CoTAA and CoTMPP, we have decided to study the behaviour of GDE catalyzed with pyrolyzed products of this compound with respect to the oxidation of SO_2.

EXPERIMENTAL

The catalyst is prepared by heating phtalodinitrile together with cobalt nitrate according to a method described in [14]. The product is dissolved in 96 %wt. H_2SO_4, followed by precipitation onto active carbon "Norit-NK" (specific surface 650 m^2.g^{-1}, according to BET), and cooling the solution in an ice-water mixture [5]. The next steps are drying and subjecting to pyrolysis in argon atmosphere for 5 hours at temperatures within the range between 600 and 900°C. Thus active carbon, catalyzed with 1 – 20 % wt. pyrolyzed phtalocyanine, is obtained, and further on, used for the preparation of GDE. The later are of double-layer type: a porous gas supplying layer and a porous catalytic layer. The binder is PTFE which was previously precipitated upon acetylene black [15].

The electrochemical characteristics of the electrodes are determined by tracing the stationery galvanostatic voltage-current relationships (E-i), and by long term tests. The measurements are carried out in a specially designed electrolytic cell, comprising a cathode, prepared from tungsten carbide, PTFE and Na_2SO_4 [16]. 4.5 N H_2SO_4 is used as electrolyte. The

---

* To whom all correspondence should be sent:
E-mail: kpetrov@bas.bg

ΔE-i curves are traced under the condition that the electrodes are supplied either with pure SO_2 or with gas mixture of SO_2 +Ar. The gases are fed to the gas supplying layer without overpressure. The potential of the electrodes is recorded vs. Hg/Hg_2SO_4 reference, recalculating data vs. NHE in the same electrolyte. The results from these measurements are used for plotting of the E-i curves in normal and semi-logarithmic coordinates as well as the ΔE -i relationships. ΔE is defined as difference between the stationary potentials at identical current densities from polarization curves of the same electrode, traced in pure SO_2 (E_{SO2}), and in gas mixture, Ar + 20 % vol. SO_2 (E_{Ar+SO2}), so $\Delta E = E_{SO2} - E_{Ar+SO2}$. The former are used for evaluation of the activity of the catalyst, while the later provide a criterion for the transport hindrances in the electrodes [17].

RESULTS AND DISCUSSION

The composition of the catalyst is optimized with respect to the parameters which determine its activity, the amount of CoPc and the temperature of pyrolysis [5, 18]. The voltage – current relationships of a set of electrodes, containing different quantities of CoPc are shown on Fig. 1. It can be noted that the characteristics of the electrode, containing 20 % wt. pyrolyzed catalyst, are practically identical to that of electrodes catalyzed with 10 % wt. This finding provides us with a foundation to continue further studies with electrodes prepared from "Norit-NK" + 10 % wt. pyrolyzed CoPc.
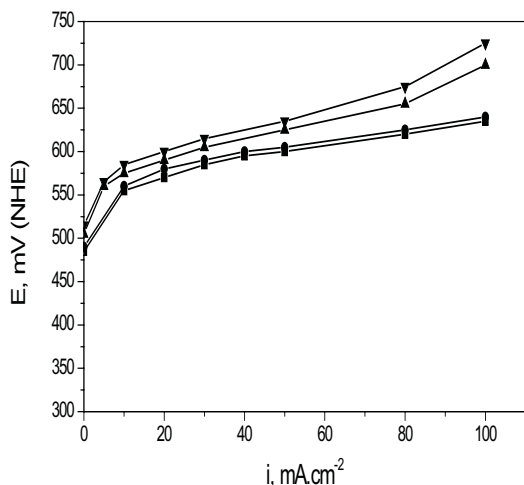
The dependence of catalytic activity on pyrolysis temperature is studied with electrodes activated with the above mentioned amount of CoPc within the temperature range of t^o = 600–900°C. The polarization curves of a set of electrodes with catalyst pyrolized at different temperatures are shown in Fig.2. The catalyst treated at 600°C is partially pyrolyzed [5] which explains the higher polarization of these electrodes. The best characteristics show the electrodes with CoPc pyrolyzed at 700°C in comparison with those, treated at higher temperatures. Similar dependence has been established for reduction of oxygen in sulphuric acid solutions [5]. In this case also, carbon catalysed with
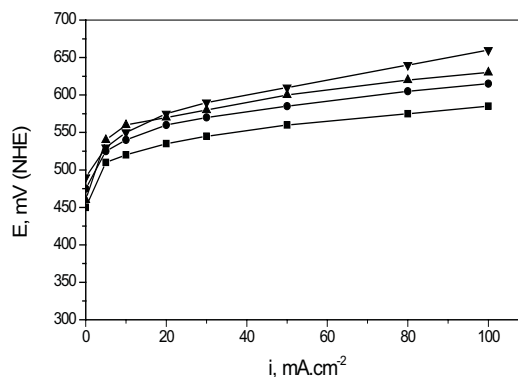
Fig. 2. Voltage – current characteristics of the GDE catalyzed with 20 mg.cm^{-2} catalyst "NORIT NK" + 10 wt. % CoPc, pyrolyzed at different temperatures: (■) - $T_{pyr.}$= 600°C; (●) - $T_{pyr.}$= 700°C; (▲) - $T_{pyr.}$= 800°C; (▼) - $T_{pyr.}$= 900°C; 4.5 N H_2SO_4, T = 20°C.

Fig. 1. Voltage – current characteristics of the GDE catalyzed with different amounts of CoPc, pyrolyzed at 900°C: (■) - 20mg/cm^2 catalyst "NORIT NK" + 1 wt. % CoPc; (♦) - 20 mg.cm^{-2} catalyst "NORIT NK" + 5 wt. % CoPc; (▲) - 20 mg.cm^{-2} catalyst "NORIT NK" + 10 wt. % CoPc; (▼) - 20 mg.cm^{-2} catalyst "NORIT NK" + 20 wt. % CoPc ; 4.5 N H_2SO_4, T = 20°C.
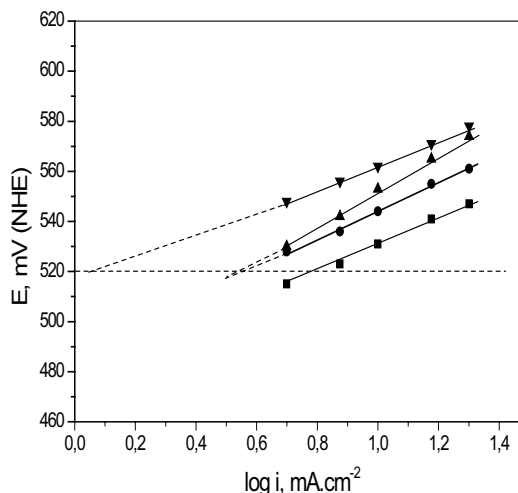
Fig. 3. Voltage–current characteristics in semi–logarithmic coordinates at low current densities of the electrodes in Fig. 2.

CoPc pyrolyzed at 700°C displays enhanced activity.

The reasons for this temperature phenomenon could be two: a change in the activity of the catalyst

190

itself and/or alteration of the transport hindrances within the complex "Norit-NK" + pyrolyzed CoPc due to the different distribution of the catalyst in the pores of the carbon carrier. The effect exerted by each of these factors is estimated from the initial polarization curves at low current densities (up to i = = 20 mA.cm^{-2}) and the ΔE-i relationships.

Fig. 3 shows the initial polarization curves. The Tafel plots provide evidence that transport hindrances in the electrodes are of minor importance within this current density range. The slopes of the straight lines are approximately 50 mV/dec in the case when CoPc is pyrolyzed at t^o=700°C or more elevated temperature. When CoPc is thermally treated at t^o = 600°C (temperature at which the pyrolysis of the chelate complex is not complete [5]) the Tafel slope is 75 mV/dec. Higher values of the Tafel slope (90–100 mV/dec) have been reported by Tarasevich and Radyushkina [7] for CoPc with no thermal treatment, deposited onto pyrographite.

The segments, cut by the Tafel plots, from the abscises at a given potential within the region of small polarizations (E = +500 mV NHE) are a criterion for the activity of the complex "Norit-NK" + pyrolyzed CoPc in a real GDE [19]. Fig. 3 shows that the highest activity is reached with electrodes containing a catalyst pyrolyzed at t^o=700°C. Higher pyrolysis temperature leads to reduced activity. The data are not relevant to the evaluation of the activity of the electrode catalyzed with CoPc pyrolyzed at t^o=600oC since the respective slope is different from the rest.
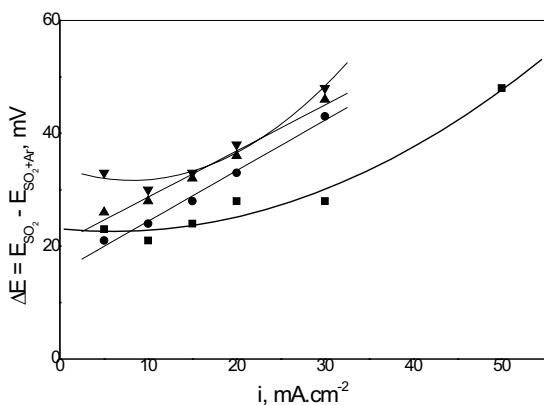
pronounced hindrances. These variations probably are due to the different distribution of the pyrolyzed catalyst in the pores of the carbon carrier, respectively various structures and different hindrance patterns.

It can be concluded on the basis of the experimental results (Fig. 3 and 4) that the good characteristics of the electrodes catalyzed with CoPc pyrolyzed at t^o = 700°C are due to both: the high activity of the "NORIT NK" – pyrolyzed catalyst complex and the reduced transport hindrances for SO$_2$ in it.

Long term tests were carried out, using electrodes catalyzed with CoPc pyrolyzed at 700°C and 900°C. Fig. 5 shows the different pattern for the increase of polarization with time. The electrodes catalyzed with CoPc pyrolyzed at 700°C shows a deterioration of its characteristics during the initial 100 – 150 hours and further on the changes are slight. The other type of electrodes displays a continuous increase of polarization and at the end of the 500 hour test-run it reaches 200 mV, rendering them practically unusable. The periodically monitored voltage – current curves at low current densities and the ΔE – i relationship of these electrodes offer a possibility to explain the reasons wich have lead to the observed increase of polarization. Fig. 6 presents the initial and final Tafel curves for both types of electrodes. It can be noted that the segments cut on the abscissa for each type are slightly affected, hence the activity of the catalyst pyrolyzed at 700°C and 900°C shows only
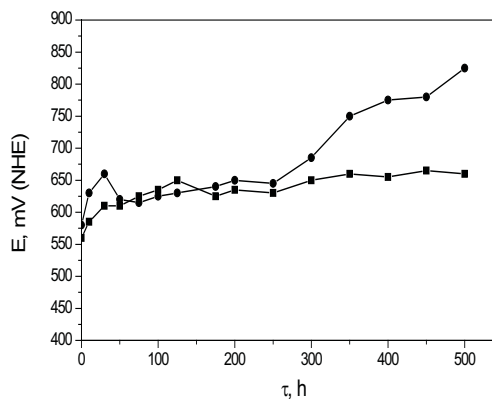

Fig. 4. ΔE - i curves of the electrodes in Fig. 2.

Fig. 5. Long term tests of GDE catalyzed with 20 mg.cm^{-2} catalyst "NORIT NK" + 10 wt. % CoPc, pyrolyzed at different temperatures: (■) - T$_{pyr.}$= 700°C; (●) - T$_{pyr.}$= 900°C; i = 60 mg.cm^{-2}, 4.5 N H$_2$SO$_4$, T = 20°C

Fig. 4 shows the ΔE -i relationships. It can be noted that at all current densities the ΔE, hence the transport hindrances, in the electrode catalyzed with CoPc pyrolyzed at t^o=700°C are the least. Electrodes containing partially pyrolyzed catalyst (t^o= 600°C) or thermally treated at temperatures exceeding 700°C display substantially more

minor changes following 500 hour test operation at 60 mA.cm^{-2}. The comparison of the ΔE - i relationship, however, provides evidence that the transport hindrances in both electrode types have

191

increased (Fig. 7). A close look at the figure reveals that: (i) for the electrode with the catalyst pyrolyzed at 700°C this increase is more substantial during the initial 125 hours; (ii) at the end of the 500 hour test the transport hindrances in electrodes with catalyst pyrolyzed at 900°C are more pronounced.
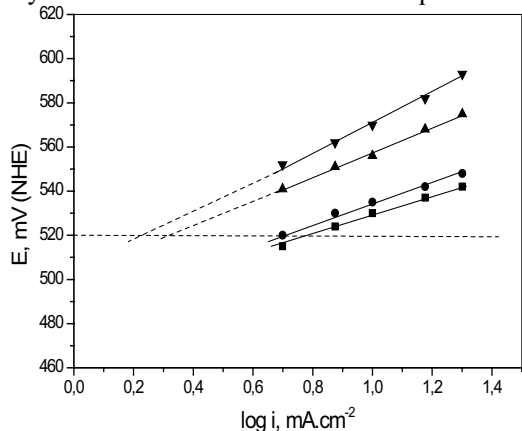

.

Fig. 6. Voltage – current characteristics in semi – logarithmic coordinates at low current densities of the electrodes subjected to long term tests: 1 -initial ; 2 - after 500 hours operation at i = 60 mg.cm^{-2}.
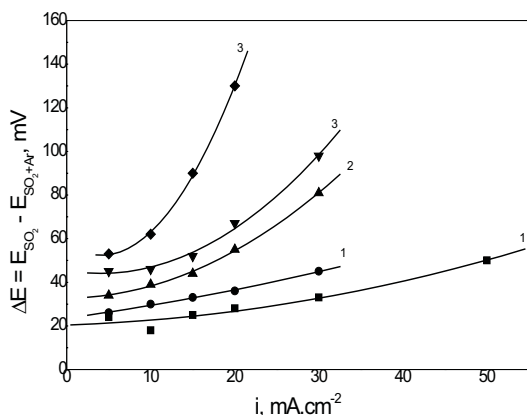

Fig. 7. ΔE - i curves of the electrodes subjected to long term tests: 1- initial; 2 - after 125 hours operation at i =60 mA.cm^{-2}; 3- after 500 hours operation at i = 60 mg.cm^{-2}.

These experimental results explain the electrode behaviour during the long term tests. The conclusion, based on such results, is that the most suitable pyrolysis temperature for CoPc, used for preparation of a catalyst for the oxidation of sulphur dioxide, is t^o =700°C.

A comparison with our previously reported results [2] shows that the long term characteristics of GDE, catalyzed with CoPc, pyrolyzed at 700°C, are superior to those of GDE, containing CoTAA and CoTMPP.

CONCLUSION

The investigated GDE, catalyzed with CoPc pyrolyzed at t^o = 700°C provide adequate perfor-

mance and can be used as anodes for oxidation of sulphur dioxide in sulphuric acid solutions.

NOMENCLATURE

CoTAA – Dibenzo-cobalt-tetra-azaanulene
CoTMPP – Cobalt tetra-methoxy-phenyl-porfirine
MC – Modified active carbon
CoTPP – Cobalt-tetra-phenyl-porfirine
CoPc – Cobalt-phtalocyanine

REFERENCES

1. W. Lu and R. L. Ammon, *J. Electrochem. Soc.*, **127**, 2610 (1980).
2. K. 2. K.Petrov, I. Nikolov and T. Vitanov, *Int. J. Hydrogen Energy,* **9**, 901 (1984).
3. H. Hiller, H. Guthke and F. Beck , *D.O.S.*, **204**, 6334 (1970).
4. A.D. Adler, F. R. Longo, I. D. Finarelli , *J. Org. Chem.*, **32,** 476 (1967).
5. J. A. R. Van. Veen, G. Visser, *Electrochemica Acta*, **24**, 921(1979).
6. М. Р. Тарасевич, К. А. Радюшкина, В. С. Боготцкий, В кн. Всесоюзная конференция по механизму металических реакций. Тезисы докладов. М., Наука, т. 2. (1978) 265.
7. М. Р. Тарасевич, К. А. Радюшкина, Катализ и електрокатализ металлопорфиринам. М., Наука, (1982)
8. К. А. Радюшкина, М. Р. Тарасевич, Електрохимия , 22 (1986) 1155.
9. Q. Jiang, H. Ketamo, A.J. Niskanen, J. Suomi, M. Håkansson, S. Kulmala,.*Electrochimica Acta,* **51**, 3332 (2006).
10. E.-G. Jäger, M. Rudolph, *J. Electroanal.Chem.*, **434**, 1 (1997).
11. Uehara, M. Kasuno, T. Okugaki, Y. Kitatsuji, O. Shirai, Z. Yoshida, S. Kihara, *J. Electroanal. Chem.*, **604**, 115 (2007).
12. M. Håkansson, Q. Jiang, M. Helin, M. Putkonen, A.J. Niskanen, S. Pahlberg, T. Ala-Kleme, L. Heikkilä, J. Suomi, S. Kulmala, *Electrochimica Acta*, **51**,289 (2005).
13. S. Buchmann, H.A. Mayer, B. Speiser, M. Seiler, H. Bertagnolli, S. Steinbrecher, E. Plies, *Electrochimica Acta*, **46**, 3207 (2001).
14. F. Beck ,. W. Dammert, J. Heiss, H. Hiller, R. Rolster. *Z. Naturforsch.* **28a**, 1009 (1973)
15. E. Budevski, I. Iliev, S Gamburzev, A Kaisheva, E. Vakanova, I. Mikhovski, *Commun. Dept. Chem. Bulg. Acad. Sci.*, **7,** 223 (1974).
16. Nikolov, K. Petrov, T. Vitanov, A Gushev, *Int. J. Hydrogen Energy*, **8,** 437 (1983).
17. Iliev, S Gamburtzev, A Kaisheva, I. Mrha, *J. Appl. Electrochem.*, **5** 291 (1975).
18. Iliev, S Gamburzev, A Kaisheva, *J. Power Sources*, **17,** 345 (1986).
19. A Kaisheva, I. Iliev, S Gamburzev, J. Power Sources, **13,** 181 (1984).

ПИРОЛИЗИРАН CO-ФТАЛОЦИАНИН КАТО КАТАЛИЗАТОР ЗА ОКИСЛЕНИЕТО НА СЕРЕН ДИОКСИД

К. Петров, Ив. Николов, Т. Витанов, Д. Узун, В. Огнянов[1]

Институт по електрохимия и енергийни системи, Българска академия на науките, ул. Акад. Г. Бончев, бл. 10, 1113 София, България

[1]Институт по органична химия с Център по фитохимия , Българска академия на науките, ул. Акад. Г. Бончев, бл. 9, 1113 София, България

Изследвана е каталитичната активност на пиролизен Co-фталоцианин, отложен върху активен въглен "Norit-NK" за окисляването на серен диоксид в сярно-кисела среда. Определени са оптималното съдържание на Co-фталоцианин и най-подходящата температура за катализатора. Показано е, че газово-дифузионите електроди с катализатор от Co-фталоцианин, получен при пиролиза при 700°C осигуряват работа в продължение на 500 часа при плътност на тока 60 mA.cm^{-2} и свръхнапрежение около 50 mV.