Short Communication

Tetrathiafulvalenes as Catalysts for the Reduction of Oxygen in Acid Electrolytes

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Summary

Tetrathiafulvalenes have been examined as metal-free electrocatalysts for the cathodic reduction of oxygen at monolayer carbon diffusion electrodes in sulphuric acid. The polarizability of the electrodes increases in the following order: conjugatively-connected polymeric tetrathiafulvalenes, catalyst-free electrodes, non-conjugatively-connected polymeric tetrathiafulvalenes, and monomeric tetrathiafulvalenes. Only electrodes that are covered by conjugatively polymeric tetrathiafulvalenes exhibit a better performance than the active carbon P 33 used as carrier; this fact is discussed in terms of the increased electronic catalyst conductivity.

Zusammenfassung

Tetrathiafulvalene als metallfreie Elektrokatalysatoren für die katodische Sauerstoffreduktion an Einschichtdiffusionselektroden in Schwefelsäure wurden untersucht. Die Polarisierbarkeit der Elektroden steigt in folgender Weise an: konjugiert verbundene polymere Tetrathiafulvalene, katalysator-freie Elektroden, isoliert verbundene polymere Tetrathiafulvalene und monomere Tetrathiafulvalene. Nur Elektroden, die mit konjugierten polymeren Tetrathiafulvalenen belegt sind, ergeben eine bessere Belastbarkeit als Aktivkohle P 33, die als Träger benutzt wurde, ein Fakt, der als Folge der gesteigerten elektronischen Leitfähigkeit der Katalysators diskutiert wird.

Introduction

With fuel cells operating in acid electrolytes the cathodic oxygen reduction that already requires a considerable activation energy for the transfer of the first electron to the oxygen according to eqn. (1)

$$O_2 + e^- \longrightarrow [O_2]^-_{ad} \qquad (1)$$

has to be activated by suitable catalysts. Apart from the expensive noble-metal catalysts, above all, the less expensive chelate compounds such as the phthalocyanines are most attractive [1]. Since the phthalocyanines easily enter into reversible redox reactions in one-electron steps [2], it appeared worthwhile to test other organic π-electron donors with analogous properties as catalysts for oxygen reduction.

The tetrathiafulvalenes (TTF) are known to have pronounced reversible redox properties also being easily able to release two electrons according to eqn. (2)

$$(2)$$
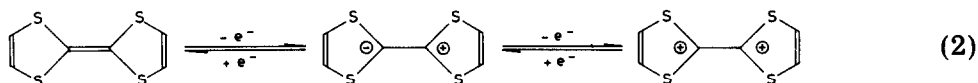
According to the substituent, the oxidation potentials* for the first step are between 0.2 and 0.6 V and between 0.65 and 0.9 V for the second step [3, 4]. Moreover, the TTF–radical salts are good solid electron conductors, a major requirement for high catalytic activity [5]. As electron donors the TTF should also accelerate the decomposition of hydrogen peroxide, thus reducing the back-potential that could build up at the cathode from the hydrogen peroxide if the oxygen has not been entirely reduced to water.

Experimental

Tests were carried out on various substituted TTF (Nos. 1, 2, 3, 7, 9 Table 1), the respective radical salts (Nos. 8, 10, 13, 14), and a TTF-dication (No. 11). Moreover, polymeric TTF were used where the TTF units had been conjugatively (Nos. 4, 5) or non-conjugatively connected (Nos. 6, 12). For synthesis of the TTF see refs. 6 - 10.

In order to obtain as large a three-phase boundary as possible at the reaction site, highly-porous carbon was used as a substrate material on which the catalysts were deposited. For this purpose, the compounds were dissolved either in chloroform (Nos. 1, 2, 3, 7, 8, 10, 12), acetonitrile (Nos. 11, 14), or concentrated sulphuric acid (Nos. 4, 5, 6)**, the carbon was added

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*In methanol/benzene (4:1); 0.1 mol/l LiCl *vs.* saturated mercury/mercury chloride electrode.

**When dissolving the TTF in concentrated sulphuric acid an oxidation takes place leading to the TTF dication (see also ref. 10). The red colour of the solution changes to green on the addition of carbon powder so that a dication reduction into monocation due to the carbon has to be assumed.

TABLE 1   195

Compounds used as catalysts

No	R_1	R_2
1	$-(CH_2)_4-$	
2	$p\text{-}CH_3OC_6H_4-$	$H-$
3	$p\text{-}C_6H_5C_6H_4-$	CH_3-
7	C_6H_5-	CH_3-

No	R_1	R_2	X^-
8	C_6H_5-	CH_3-	Br^-
10	C_6H_5-	CH_3-	$TCNQ^-$
14	$-(CH_2)_3-$		$TCNQ^-$

No	R_1	R_2	X^-
11	C_6H_5-	CH_3-	ClO_4^-

No	R_1	R_2
4	$-C_6H_4-$	$H-$
5	$-C_6H_4C_6H_4-$	$H-$
6	$-CH_2CH_2-$	C_6H_5-

No	
9	The same as 7 but synthesized on carbon P 33.
12	The same as 6 but the iodine salt.
13	The same as 8 but synthesized on carbon P 33.

and the organic solvent was distilled off or the acid was diluted with ice water. The material was then filtered off and dried for 3 h at 80 °C. In two cases (Nos. 9, 13) we carried out the synthesis of TTF from the dithiolium salt according to ref. 3:

(3)
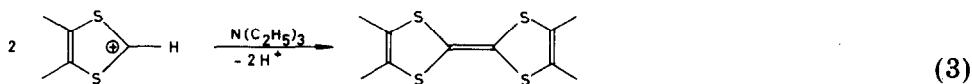
when active carbon was present in the acetonitrile.

The active substances described were stirred into water and mixed with Teflon suspension. After the Teflon had flocculated, the mixture was dried, homogenized and pressed into cylindrical tabloids 28 mm in diameter and about 4 mm thick. These electrodes normally contained 4.7% of the catalyst, 15% Teflon and 80.3% of active carbon P 33. They were mounted in such a way that, from one side, oxygen under a 2.1×10^4 Pa pressure could be forced through while the electrode could be wetted by the electrolyte (4.5N sulphuric acid) on the other side. A platinum ring on the gas side served as a conductor. Lead was used as the counter electrode and the reference electrode was brought into close proximity with the electrode by means of a

Luggin capillary. The current density–potential curves were recorded by galvanostatic means at 25 °C.

Results and discussion

As seen in Fig. 1, the majority of the TTF employed, and also the corresponding oxidized forms (mono- and dications), prove to be inefficient
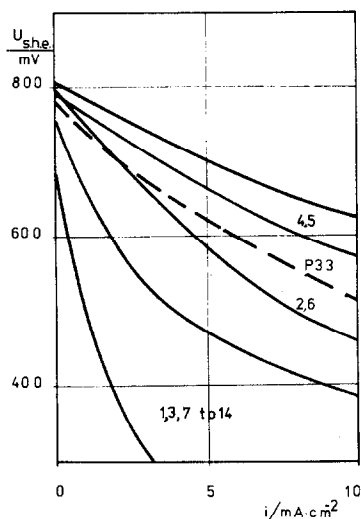

Fig. 1. Current–potential diagrams of monolayer diffusion electrodes for oxygen reduction with 4.7% catalyst (see Table 1), 80.3% active carbon P 33 and 15% Teflon, measured in 4.5N sulphuric acid with 2.1×10^4 Pa oxygen overpressure at 25 °C. Potentials $vs.$ standard hydrogen electrode.

for acceleration of the electrochemical reduction of oxygen. Also, the different methods of application of TTF to carbon show no significant influence upon the catalytic activity; the reason for this is probably that the large amount of TTF additions (5%) reduce the electron conductivity within the electrode, thus inhibiting the reduction process. The high reduction capability of TTF (that apart from its low oxidation potential is also shown by the fact that these compounds in a highly dispersed state, $e.g.$, adsorbed on silica gel or aluminium oxide, are readily oxidized by atmospheric oxygen) is not sufficient to compensate for the negative effect of low conductivity. A higher catalytic effectiveness would be expected if the intrinsic conductivity of TTF could be raised substantially. Such a rise is possible by the use of a TTF polymer in which the TTF units are conjugatively connected so that a higher electron mobility (electron delocalization) is given in the polymer molecule (see also ref. 10). Figure 1 shows that these polymeric TTF prove to be active catalysts for the oxygen reduction process. It is also obvious that the polymeric structure of the TTF alone is insufficient for a

high catalytic activity, since a non-conjugated connection of the TTF units associated with a decreased electron mobility within the polymer molecule clearly leads to a reduced activity (4.5 → 6). A further increase in efficiency of TTF as catalysts for electrochemical oxygen reduction should therefore result from the development of highly conducting polymeric TTF.

References

1 C. Kretzschmar and K. Wiesener, *Z. Phys. Chem. (Leipzig), 257* (1976) 39.
2 F. Beck, J. Heiss, H. Hiller and R. Polster, *Katalyse an Phthalocyaninen, Symposium, Hamburg 1972*, Thieme-Verlag, Stuttgart, 1973, p. 53.
3 G. Schukat, Le van Hinh and E. Fanghänel, *Z. Chem., 16* (1976) 360.
4 J. R. Lenhard, R. Rocklin, H. Abruna, K. Willman, K. Kuo, R. Nowak and R. W. Murray, *J. Am. Chem. Soc., 100* (1978) 5213.
5 J. H. Perlstein, *Angew. Chem., 89* (1977) 534.
6 A. F. Garito and A. J. Heeger, *Acc. Chem. Res., 7* (1974) 232.
7 G. Schukat, Le van Hinh, E. Fanghänel and L. Libera, *J. Prakt. Chem., 320* (1978) 404.
8 M. Marita and C. U. Pittman, *Synthesis*, (1976) 489.
9 Le van Hinh, G. Schukat and E. Fanghänel, *J. Prakt. Chem.*, in press.
10 Le van Hinh, G. Schukat, E. Fanghänel and L. Libera, *J. Prakt. Chem.*, in press.