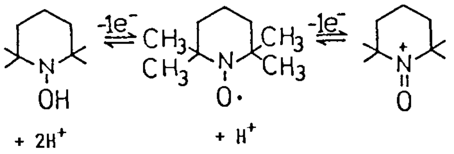
CHEMISTRY LETTERS, pp. 75-78, 1990.

A Preparative Nitroxyl-radical Coated, Graphite Felt Electrode for the Oxidation of Alcohols

Tetsuo OSA, Yoshitomo KASHIWAGI, Kenji MUKAI,
Akio OHSAWA, and James M. BOBBITT[+]
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980
[+]Department of Chemistry, University of Connecticut, Storrs
CT 06269-3060, U. S. A.

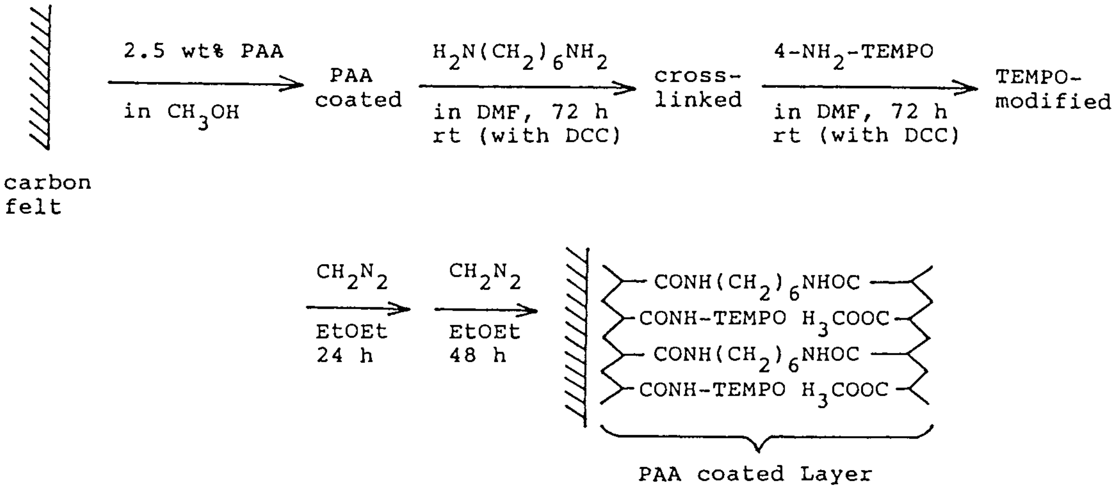
The graphite felt electrode, coated with ca. 3 wt% polyacrylic acid, was modified by successive reactions with hexamethylenediamine (for cross-linking), 4-amino-2,2,6,6-tetramethylpiperydinyl-1-oxyl (4-amino-TEMPO) and diazomethane (for methylation). Properties of the electrode, were compared with a non-crosslinked and non-methylated one, a crosslinked and a non-methylated one, and a crosslinked and incompletely methylated one; the present electrode was stable and oxidized nerol to neral selectively with turnover number > 1560.

In previous work, we,[1] as well as the group of Moutet[2] have published that graphite felt anodes coated with nitroxides act as catalysts for the oxidation of alcohols. Briefly, the nitroxides are oxidized on the surface of the anode to nitrosonium salts,[3] which serve as selective oxidizing agents. In the process, the nitrosonium salts are probably reduced to hydroxylamines which are reoxidized to nitrosonium salts to complete the catalytic cycle. However, in both reported cases, the electrode coatings were not enough stable. In this paper, we will report the preparation of a much more stable coated electrode and the electrocatalytic oxidation of nerol.



(1)

A typical preparation of the modified electrode is described as follows. The graphite felt (Union Carbide Corp., 5 x 2 x 0.5 cm^3, 450 mg) was first dipped in a 2.5 wt% polyacrylic acid (PAA) methanol solution and dried under vaccum. The coated amount of PAA was about 3 wt%. This coated electrode was then crosslinked with 30 ml of $9.38\text{x}10^{-3}$ M (M= mol·dm^{-3}) hexamethylenediamine dimethylformamide (DMF) solution (0.25 equiv. to COOH of PAA) in the presence of dicyclohexylcarbodiimide (DCC) (2 equiv. to hexamethylenediamine) for 72 h at room temperature. The electrode was then treated with 30 ml of a $3.75\text{x}10^{-2}$ M 4-amino-2,2,6,6-tetramethylpiperydinyl-1-oxyl (4-amino-TEMPO) DMF solution in the presence of DCC (1.2 equiv. to



Scheme 1. Preparation method of TEMPO-PAA modified carbon felt electrode.

4-amino-TEMPO) for 72 h at room temperature. The resulting electrode coatings were insoluble in most organic solvents and contained ca. 33% of cross-linking and ca. 52 % of nitroxide (based on the reacted COOH ratio (%) to the total COOH of coated PAA). At this point, the electrode had 15.3% free COOH group as measured by titration. The electrode was treated twice with large excess of diazomethane in diethyl ether (distilled from N,N'-dimethyl-N,N-dinitroso-tetraphthalamide by the general procedure4)) for 24 h. No COOH groups were present, although treatments were twice necessary. The methylation was carried out to block all of the remaining carboxyl groups in the layer because the carboxyl group is known to be sufficiently basic to promote the decomposition of nitrosonium salts.2,5)

Characteristics of the four kinds of TEMPO-modified electrodes are shown in Table 1. Electrode 1 is a non-crosslinked and non-methylated one as described in our previous paper;1) 2 is a crosslinked but non-methylated one; 3 is a crosslinked and once-methylated one; and 4 is a crosslinked and twice-methylated one prepared in the present study. The density of TEMPO on the electrode was determined to be 1.6 μmol per cm^3 graphite felt electrode. This value was obtained by elementary analysis and titration.

Table 1. Characterization and Oxidation Potential of TEMPO-Modified Graphite Felt Electrodes

Electrode	Ratio of COOH groups of PAA (%) Free	Cross-linked	TEMPO-modified	Methylated	Oxidation potential V vs. Ag/0.2 M AgNO$_3$
1	51	0	49	0	0.40
2	15	33	52	0	0.46
3	5.2	33	52	10.1	0.56
4	0	33	52	15.3	0.84

The cyclic voltammetry (CV) of electrodes 1-4 was carried out using a working electrode (1 x 1 x 0.5 cm^3) in a 0.2 M NaClO$_4$/CH$_3$CN solution. The potential of the

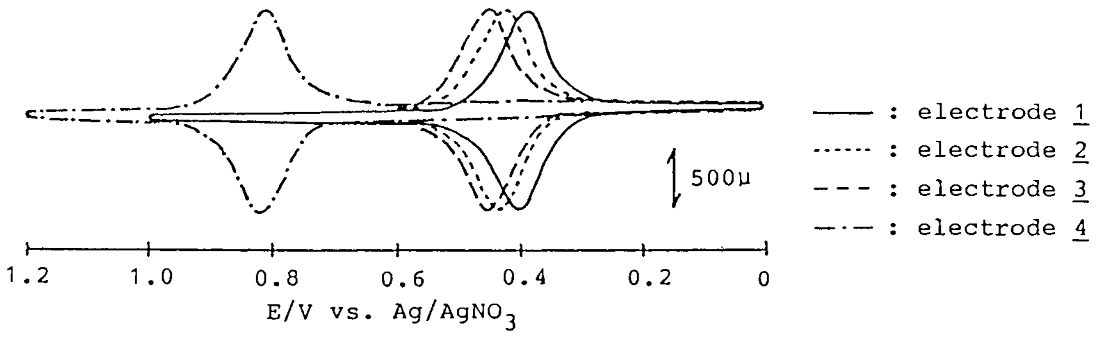


Fig. 1. Cyclic voltammograms of electrode 1-4 in 0.2 M $NaClO_4/CH_3CN$ at scan rate of 10 mV s^{-1}.

working electrode was recorded against a reference electrode Ag/0.2 M $AgNO_3$. In all cases, the nitroxide-nitrosonium couple was clearly present and reversible as seen in Fig. 1. Although the CV curves looked alike in all cases, the potential was shifted anodically as the carboxyl groups were successively eliminated, as shown in Fig. 1 and Table 1. There is no apparent reason for this large shift. N-Acetyl-4-amino-TEMPO showed a reversible wave at 0.68 V and could be recovered unchanged from a treatment with diazomethane, showing that the nitroxide was not changed by methylation. The potential shift is clearly related to the removal of carboxyl groups, since cross-linking by amide formation causes a slight shift (0.40 V to 0.46 V in CH_3CN) while the two successive methylations cause a shift from 0.46 V (15.3% carboxyl before methylation) to 0.56 V (5.2% carboxyl) and to 0.84 V (0.0% carboxyl). A change is surface pH would be expected as the carboxyl groups were methylated, from ca. 4.2 (as measured for acrylic acid) to perhaps 7 but this could account for only a shift of 0.170 V, according to a Nernstian calculation, whereas the actual shift is 0.44 V. The surface is certainly more lipophilic after methylation, but it is not clear why this would shift the potential so much.

The next interesting result is that the electrode surface is made much more stable by cross-linking and methylation. The preparative, potentially controlled electrolysis was performed in an CH_3CN solution using an H type divided cell separated by cationic exchange membrane (Nafion 117). For electrodes 1-3, the anolyte was 40 ml CH_3CN containing 3 mM nerol, 3 mM tetralin as a gas chromatography standard, 6 mM 2,6-lutidine and 0.2 M $NaClO_4$. For 4, the anolyte contained 15 mM nerol and 15 mM tetralin in expectation of a higher consumption of nerol due to a higher catalytic activity of 4. In all cases, the catholyte was 40 mM CH_3CN containing 0.2 M $NaClO_4$ and 1 ml 1,2-dibromoethane. Controlled electrolysis was carried out at +1.2 V on 4 and at +0.8 V on 1-3. During electrolysis, the sample for gas chromatography (PEG 20/raising temp 4 °C min^{-1} from 160 to 220 °C, inj. temp 260 °C) was taken from the electrolyte at appropriate intervals and analyzed.

The results of gas chromatography are shown in Fig. 2. The current efficiency for formation of neral is over 90%, and no by-products were observed (100% selectivity). The electrocatalytic activity of 1-4 for consumption of nerol and formation of neral is the order of $4 \gg 3 > 2 > 1$. It is clear that 4 is much more stable than the one previously reported.$^{1)}$

Secondary alcohols were also oxidized to the corresponding ketones under similar conditions. For instance, cyclohexanone was obtained from cyclohexanol on 2 by 62% of current efficiency, 57% of selectivity and 148 of turnover number. It means that 2,6-lutidine acts as a base catalyst in this system, differing from the result reported by Semmelhack et al.6)

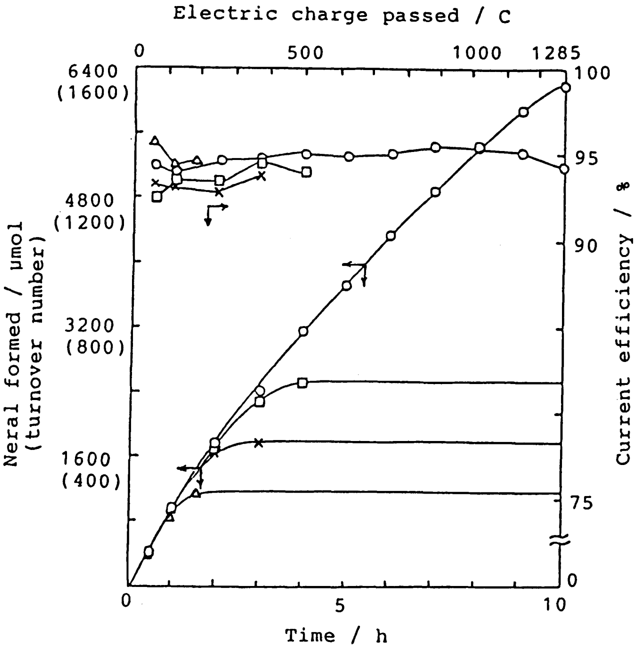
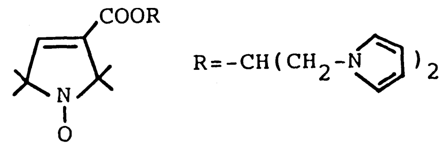


Fig. 2. Macroelectrolysis of nerol on electrodes 1-4. Turnover number is given by 2 x mol of neral/mol of TEMPO. △ : 1, × : 2, □: 3, ○: 4.

Moutet2) has reported the preparation of 2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl modified carbon felt electrodes and the electrocatalytic oxidation of several alcohols. The electrode was prepared by electropolymerization of the monomer 5 on carbon felt. They reported that the instability of their electrode and the higher coverage of electropolymerization layer on the carbon felt electrode reduced the diffusion of substrate and base molecules. The use of Na_2CO_3 as a base gave better results than that of collidine which decomposes the polymer layer. Our electrode differs not only in the structure of nitroxyl-radical, but also in the kind of polymer, and is stable to collidine or 2,6-lutidine. The turnover number (ratio mol of coulomb passed x 2/mol of nitroxyl-radical) for neral oxidation on our electrode is larger than 1560, whereas their number is ca. 400 for p-methoxybenzyl alcohol.



5

We are now trying to clarify the inactivation mechanism of the TEMPO nitroxyl-radical and to prepare more catalytically active electrodes for preparative electrooxidation of organic compounds.

References

1) T. Osa, U. Akiba, I. Segawa, and J. M. Bobbitt, Chem. Lett., 1988, 1423.
2) A. Deronzier, D. Limosin, and J-C. Moutet, Electrochimica Acta, 32, 1643 (1987).
3) J. M. Bobbitt and M. C. L. Flores, Heterocycles, 27, 509 (1988).
4) F. Arndt, Org. Synth., Coll. Vol. II, 164 (1943).
5) G. Moad, E. Rizzardo, and D. H. Solomon, Tetrahedron Lett., 22, 1165 (1981).
6) M. F. Semmelhack, C. S. Chou, and D. A. Corted, J. Am. Chem. Soc., 105, 4492 (1983).

(Received October 2, 1989)