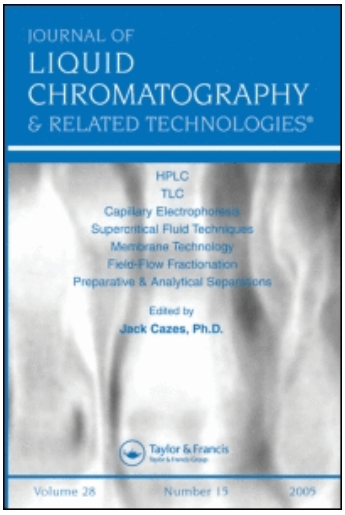

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CARBON COMPOSITE ELECTRODES FOR LIQUID CHROMATOGRAPHY/ELECTROCHEMISTRY: OPTIMIZING DETECTOR PERFORMANCE BY TAILORING THE ELECTRODE COMPOSITION

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ABSTRACT

Results obtained in this laboratory and elsewhere suggest that carbon composite electrodes may possess a signal-to-noise (S/N) advantage compared to continuous electrodes such as glassy carbon when used for detection of analytes in flowing streams. One such composite electrode which appears particularly attractive in this regard is the Kel-F-graphite (Kelgraf) electrode, compression molded from Kel-F and powdered graphite and containing 5 to 30% graphite by weight. Studies of the electrode surface by scanning electron microscopy and X-ray photoelectron spectroscopy in conjunction with electrochemical investigations employing chronoamperometry, cyclic voltammetry, and capacitance measurements have led us to view the electrode surface as an ensemble of microelectrodes, the dimensions of which can be varied by changes in particle size and/or ratio of Kel-F to graphite in the composite. The S/N advantage of the composite electrode apparently arises from a signal (current) enhanced by radial diffusion of analyte to the individual microelectrodes, resulting in a response greater than that obtained from a continuous electrode of equal active area. Since detector noise is generally assumed proportional to the active area of the electrode, S/N enhancement results.

For composite electrodes employed in a thin-layer channel design LC detector, the observed variations in the S/N ratio with changes in (1) composite composition (%C), (2) particle

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size of Kel-F used in fabrication of the composite, and (3) area of composite exposed in the flow channel are discussed within the context of the microelectrode ensemble model. It is further demonstrated that the ability of the electrode to resist fouling can be modified by variation in composite composition.

INTRODUCTION

A variety of electrode materials have been incorporated into the design and construction of flow-through electrochemical (EC) detectors, including many forms of carbon (1-6). For liquid chromatography with electrochemical detection (LCEC), the detector electrode material should be compatible with a variety of solvents and organic modifiers, useful over a large potential range, and easy to fabricate or machine into the desired configuration at reasonable cost. Carbon is an attractive electrode material which meets most of these criteria. Indeed, numerous EC detectors have incorporated working electrodes made of various forms of solid carbon or graphite, including glassy carbon (2,7), highly oriented pyrolytic graphite (8), low-temperature isotropic carbon (9), reticulated vitreous carbon (4,10,11), and carbon cloth (6,12). Many other detectors have employed carbon or graphite particles either in packed beds (13) or mixed with a binder such as Nujol (1), silicone rubber (14,15), ceresin wax (16), polypropylene (17), polyethylene (3), Teflon (18), or Kel-F (5,19,20,21). This latter group of electrodes in which carbon particles are mixed with a binder shall be referred to as composite electrodes, the most popular of which is undoubtedly the carbon paste electrode (1).

The Kel-F-graphite (Kelgraf) composite electrode developed in our laboratory (19) possesses several advantages compared to either solid carbon (e.g., glassy carbon) or other composite electrodes (5,19,20). Fabrication of the Kelgraf electrode consists of mixing Kel-F (polychlorotrifluoroethylene) particles and powdered graphite in the desired weight proportion (typically 5-30% graphite) and compression molding the mixture in a steel die using a heated laboratory press (the type used in preparing KBr pellets for IR analysis) (19,22). The resulting composite (Kelgraf) is essentially a conducting

plastic which retains many of the properties of Kel-F itself. As a result, Kelgraf is more easily fabricated or machined into the desired configuration than are solid carbon materials and, unlike most carbon paste electrodes, is virtually impervious to the organic solvents and modifiers encountered in liquid chromatography.

In surveying the LCEC literature, one perceives that EC detectors employing composite electrodes rather consistently produce higher signal-to-noise (S/N) ratios than do detectors employing continuous electrodes such as glassy carbon (23). Admittedly, rigorous comparisons under controlled conditions of the S/N behavior of various electrode materials are lacking and such studies are being initiated in this laboratory. Nonetheless, composite electrodes used in flowing stream detectors appear to us to possess an inherent S/N advantage.

In an earlier report the S/N behavior of the Kelgraf electrode was shown to depend on the composite composition (5) and it was proposed that the lateral diffusion regime around small isolated active sites on the composite surface leads to steady-state current response on liquid chromatographic flow time scales, resulting in partial flow noise immunity (5). It was further suggested that variations in composite composition produced corresponding variations in active and inactive site sizes which were responsible for the observed S/N dependence (5). However, experimental data verifying a link between electrode composition and active and inactive site sizes were not available at that time.

More recent studies confirm that the Kelgraf composite electrode (and most likely other composites as well) behaves as an ensemble of microelectrodes, the dimensions of which can indeed be adjusted by variations in composite composition and/or particle size of Kel-F used in the fabrication (22). Radial diffusion at individual microelectrodes results in an enhanced analytical signal compared to a continuous electrode of equivalent active area (22). Since noise is generally taken to be proportional to active electrode area (7,17), a composition-dependent S/N advantage is predicted.

In this report, the observed variations in the S/N ratio of a thin-layer channel-type EC detector with changes in composite electrode composition (% graphite), particle size of Kel-F used

in fabrication of the composite electrode, and area of composite electrode exposed in the flow channel are discussed within the context of the microelectrode ensemble model. It is further demonstrated that the ability of the electrode to resist fouling can be modified by variation in composite composition.

MATERIALS

The p-methoxyphenol (Eastman) and resorcinol (Baker) were crystalline materials with no visible discoloration and were used as received. Reagent grade $NaH_2PO_4 \cdot 3H_2O$ (Baker) was dried at 100°C for 24 hr. to remove the water of hydration and was used without further purification. The water used for the preparation of LC eluents was purified as described previously (5) and the HPLC grade acetonitrile (Burdick and Jackson) was used as received.

The powdered graphite ("F" purity, Ultracarbon Corp., Bay City, MI) used in fabrication of the electrodes had a particle size of <1 μm. The Kel-F-81^R (3M Corp., St. Paul, MN) had a particle size after sieving of ca. 150-450 μm. The 19-00 wax (polychlorotrifluoroethylene, i.e., Kel-F, Halocarbon Products Corp., Hackensack, NJ) had a particle size after sieving of <75 μm.

METHODS

The HPLC system and the electrochemical detector utilizing the Kelgraf electrode have been described in detail elsewhere (5,20).

Electrodes

Disk electrodes for the EC detector were fabricated as described previously (19,22). Three series of electrodes of 5, 10, 15, 20, and 25% carbon were fabricated. The first series used Kel-F-81 as the binder and were fabricated without degassing the composite mixture before compression molding (19). For the higher carbon compositions this resulted in voids

on the surface (visible under ca. 50X magnification) and throughout the composite which had a detrimental effect on the performance of the electrode (see discussion below). These electrodes, hereafter referred to as 3M-A electrodes, were fabricated with an insulating Kel-F sheath surrounding a center core of Kelgraf. The geometric area of conducting Kelgraf exposed in the flow channel varied somewhat from electrode to electrode, but it was ca. 20 mm^2 for all electrodes in the 3M-A series.

The second series of electrodes was also fabricated with Kel-F-81, but in this case the degassing step (22) was employed. In this series no voids were visible on the surface of any of the electrodes. The entire electrode disk was made of Kelgraf (no sheath) so the geometric area exposed in the flow channel was defined by the area of the channel itself (61 mm^2). These electrodes will be referred to as 3M-B electrodes. This series also included a 30% electrode.

The third series of electrodes was fabricated by the same procedure as the 3M-B series (22) except that the 19-00 wax was employed as the binder instead of the Kel-F-81. These electrodes will be referred to as HC electrodes. A 30% electrode was not fabricated for this series and the 5% HC electrode had such a high resistance (>1kΩ) that it was not used in this study.

RESULTS AND DISCUSSION

In trace analysis employing LCEC, one performance characteristic which is of considerable importance is the detection limit, defined here as the amount of injected analyte which produces a signal-to-noise (peak-to-peak) ratio of two. In principle, detection limits can be improved (lowered) by enhancing the signal (current) obtained from a given amount of analyte and/or reducing the system noise. Assuming the detector electrode is maintained at a potential such that the current is mass transfer limited, then signal enhancement can be achieved by increasing the flux of analyte to the electrode surface. If flow through the detector is laminar and if migration is negligible, then analyte is transported to the electrode by

convective diffusion. The limiting current at a conventional channel type electrode is then given by (17)

$$I = 1.467\ nFCW_e\ [\frac{DL}{b}]^{2/3}\ [\frac{\bar{U}}{W_c}]^{1/3} \qquad (1)$$

where W_e and L are the width and length, respectively, of the continuous electrode, b is the channel thickness, $\bar{U}$ is the average volume flow rate, W_c is the width of the channel, C is the concentration of analyte in the bulk solution, D is the diffusion coefficient, and n and F have their usual electrochemical definitions. Equation 1 indicates that flux to the electrode, and hence analytical current, can be increased by decreasing the channel height (thickness of the solution layer adjacent to the electrode) and/or increasing the volume flow rate. Both of these approaches, however, have practical limits. For example, planarity of electrode and cell surfaces limit the smallness of b and chromatographic considerations (resolution, backpressure, etc.) as well as the desire to maintain laminar flow through the detector restrict the range of $\bar{U}$. It should also be noted that an increase in L does not produce a proportional increase in signal (eq 1), a result of the depletion effect which is manifested by an increase in diffusion layer thickness at downstream portions of the electrode. In fact, increasing L may lead to a degradation in the S/N ratio (see discussion below).

Reducing detector noise can also lead to improved detection limits. Although several different types of EC detector noise can be identified, a general theoretical treatment of such noise does not yet exist. Neglecting environmental noise which can be effectively minimized if necessary by appropriate shielding, there appear to be three major sources of noise in an EC detector: electronic noise due principally to voltage fluctuations in the control amplifier of the potentiostat (7); chemical noise attributed to incomplete wetting of the electrode surface which causes variations in eluent flow path across the electrode and also to the porosity of the electrode material and to localized turbulance due to surface roughness (5,7); and flow noise (pump noise) synchronized with the stroke of a piston-type LC pump (24). Both electronic and chemical

noise appear to be random and proportional to electrode area (7,17) and when such noise dominates, increasing electrode area (by increasing L for example) can actually degrade the S/N ratio. Indeed, a reduction in the electrode area has been suggested for reducing noise and increasing the S/N ratio (17). Flow noise due to variations in $\bar{U}$ should exhibit the same dependence on the electrode area as the signal (eq 1), and changes in the area of a continuous electrode should have little effect on the S/N ratio when flow noise dominates. Decreasing electrode area to increase S/N and thus improve detection limit has an obvious limit. Greater amplification of the small currents would be required and eventually noise in the current follower and subsequent amplification system would become limiting.

Work in our laboratory suggests that composite electrodes may possess an inherent S/N advantage compared to continuous electrodes such as glassy carbon. To a first approximation, a composite electrode may be viewed as an array of microelectrodes as depicted in Figure 1. The dimensions of the microelectrodes and of the insulating regions separating the microelectrodes can be controlled by the size of graphite particles, the weight percent graphite, and in the case of Kel-F binder, the particle size of the binder used in fab-

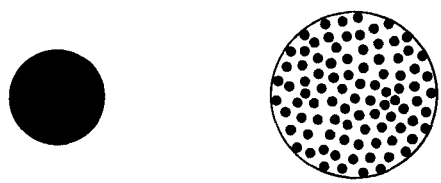

Figure 1. Comparison of a continuous electrode (e.g., glassy carbon) and an ensemble of microelectrodes (e.g., Kelgraf Composite) having the same active area. Ag and Ac represent the active areas of the glassy carbon and composite electrodes, respectively, with Ag = Ac. Qg and Qc represent the geometric areas of the glassy carbon and composite electrodes, respectively, with Qc > Qg.

rication of the composite (22). With the Kelgraf electrode, each active region or microelectrode on the surface is actually an aggregate of small carbon particles (22), and such is probably the case with many other composites as well. However, one feature of the Kelgraf electrode which distinguishes it from other composites is the relatively low carbon content of the composite, typically ca. 15%, resulting in a proportionately low active area (corresponding to conducting graphite on the surface) relative to the geometric area (22).

Radial diffusion contributes significantly to the current obtained with electrodes of very small diameter (25). With an ensemble of microelectrodes (e.g., a composite electrode), one would expect to obtain a time dependent enhancement of the current relative to that obtained from a continuous electrode of equal active area. Indeed, we have demonstrated by means of chronoamperometry that the apparent area of a Kelgraf electrode varies from the true active area at very short measurement times (a few milliseconds) to something approaching geometric at longer measurement times (a few seconds) (22). As mentioned earlier, one way of enhancing the analytical signal of an EC detector is to enhance the flux of analyte to the electrode surface. In effect, reconfiguring a continuous electrode (e.g., glassy carbon) into an ensemble of microelectrodes (e.g., Kelgraf composite) as depicted in Figure 1 results in an enhancement of flux, and thus signal, a consequence of radial diffusion. Since this is accomplished without an increase in active area and, hence, random noise, a S/N enhancement is predicted. A further enhancement of the S/N ratio can be obtained with the composite electrode (relative to the continuous electrode) if flow noise is the dominant type of noise. The composite electrode tends to be more immune to flow fluctuations than a continuous electrode, a result of the tendency of the microelectrodes to achieve steady state current response during the pump refill stroke (5). This has also been demonstrated for a channel-type EC detector employing a carbon fiber array electrode (26).

To estimate the degree of S/N enhancement which might be obtainable, we have applied a modification of the model of Matsuda et. al (27) for partially blocked electrodes to the calculation of the chronoamperometric response of Kelgraf com-

posite electrodes (22). For residence times of 0.2-0.4 s for analyte adjacent to the electrode surface of our detector (5), an enhancement in S/N of ca. 2-3 is predicted for composites similar to the 15% 3M-A and 3M-B electrodes and ca. 5 for composites similar to the 15% HC electrodes, assuming noise is proportional to active area (22). These results also assume that the relative enhancement of flux resulting from radial diffusion is independent of convection, an approximation to be sure.

Since the active and inactive site dimensions of the Kelgraf composite electrode can be varied (22), it should be possible to optimize the S/N ratio of these detector electrodes. As the carbon content of the composite increases, the surface of composite electrodes approaches that of a continuous carbon electrode, neglecting specific effects of the binder (28), and the S/N advantage diminishes. For this reason, composite electrodes with relatively high carbon content may not be as advantageous as those with lower carbon content. Indeed, a carbon paste electrode (ca. 60% C) displays a S/N of approximately one-half that of a 25% 3M-A Kelgraf electrode (29). On the other hand, as carbon content (hence, active area) decreases, the resistance of the electrode increases, leading to increasing electronic noise (30) which, when coupled with the higher gain necessary to measure the smaller current, should lead to a deterioration of S/N.

Figure 2 illustrates the dependence of the sensitivity (signal normalized with respect to concentration)-to-noise ratio on composition for the three series of Kelgraf electrodes employed in a channel-type flow-through EC detector. In each case, the S/N decreases as graphite content increases beyond 15%. Visible voids on the surface of the 20% and 24% 3M-A electrodes (see experimental section) probably account for the exceptionally low S/N for those electrodes, since such voids appear to increase noise (7). Table I displays the observed signal and noise for each electrode where it is noted that, although active electrode area decreases proportionately with %C (22), the signal does not decrease proportionately with %C. We believe this to be due to the smaller sizes of the microelectrodes at lower %C (22) and a current enhancement resulting from increased radial diffusion at these smaller

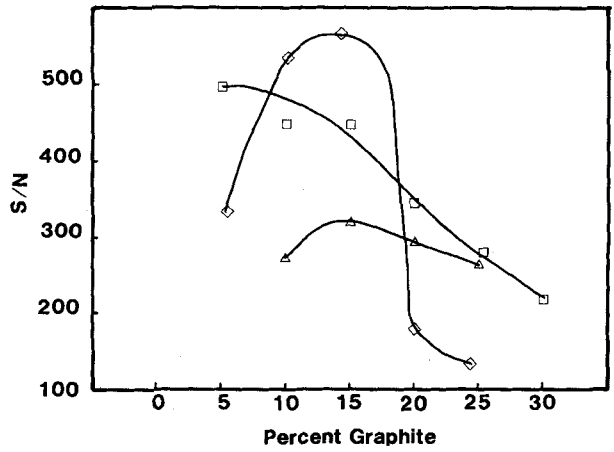

Figure 2. Variation in the S/N ratio with percent graphite for the three series of electrodes. ◇ = 3M-A electrodes; □ = 3M-B electrodes; △ = HC electrodes.

active sites. Similarly, the consistently larger signals obtained from the HC electrodes (Table I) compared to the 3M-B electrodes (equal areas exposed in the flow channel) result from the smaller active site sizes of the HC electrodes (22).

The variation of noise with composite composition is also very interesting. Unless noted otherwise, the noise (Table I) was random, presumably consisting of electronic and chemical contributions. As noted earlier, such noise is believed proportional to active area of the electrode (7). With the 3M-A electrodes, random noise decreased with decreasing active area (% carbon) until flow noise became dominant, at which point noise was insensitive to further changes in composite composition. At lower carbon content, the average dimensions of the inactive region between microelectrodes is relatively independent of composition (5,22). Since separation of microelectrodes is an important factor governing flow noise immunity (5,26), the observed dependence of noise on composition for the 3M-A electrodes can be rationalized.

The noise observed with the 3M-B electrodes was random throughout the range of compositions studied, which we attribute to the larger geometric area (ca. 3X) exposed in the flow channel with the 3M-B electrodes compared with the 3M-A elec-

Table I

Signal and Noise as a Function of Electrode Composition

Electrode Series	Composition (%C)	Signal[a] (nA/μM)	Peak-to-Peak Noise (pA)	S/N
3M-A[b]	24.3	20	150	130
	20.0	18	100	180
	14.3	17	30[d]	570
	10.2	16	30[d]	530
	5.4	10	30[d]	330
3M-B[c]	30.0	76	350	220
	25.3	70	250	280
	20.0	69	200	350
	15.0	67	150	450
	10.0	56	125	450
	5.0	50	100	500
HC[c]	25.0	79	300[d]	260
	20.0	88	300[d]	290
	15.0	81	250[d]	320
	9.9	68	250[d]	270

[a] p-Methoxyphenol. Signals normalized with respect to concentration but not with respect to geometric electrode area.

[b] Column: μ-Bondpak C_{18} (5 μm); E_{app} = 1.15V vs. Ag/AgCl/3.5M KCl; 0.05M phosphate buffer, pH 4.2, 25/75 (v/v) acetonitrile/water, 1.1 mL/min.; geometric electrode area ca. 20 mm^2.

[c] Column: Ultrasphere C_8 (5 μm); E_{app} = 1.25V vs. Ag/AgCl/3.5 M KCl; 0.05M phosphate buffer, pH 4.2, 40/60 (v/v) acetonitrile/water, 1.1 mL/min.; geometric electrode area 61 mm^2.

[d] Predominantly pump noise.

trodes. Thus random noise could not be reduced to a sufficiently low level to permit observation of a flow noise limit as in the case of the 3M-A electrodes. Figure 3 displays the dependence of random noise on electrode composition for the 3M-B electrodes. Random noise does indeed decrease monotonically with area (% carbon) though the dependence is not strictly linear as suggested for continuous electrodes (7). The departure from linearity may reflect the influence of other composite characteristics on the random noise, such characteristics as composite resistance and granularity. It is interesting to note that for this electrode series throughout which the

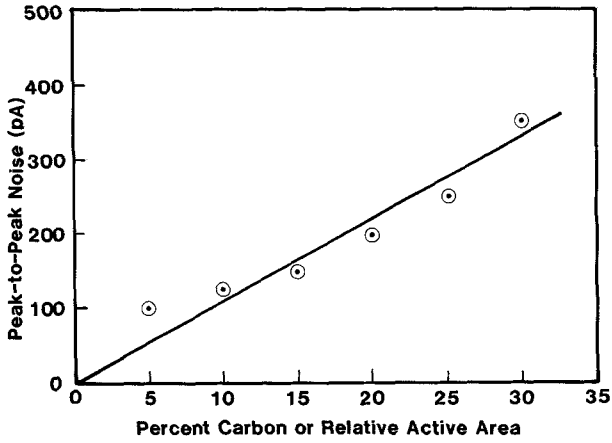

Figure 3. Dependence of random noise on percent graphite (or relative active area) for the 3M-B series of electrodes. The solid line is for reference only and has no theoretical significance.

dominant noise is random, the enhancement in S/N by a factor of two to three in going from higher carbon content (more closely approximating a continuous electrode) to lower carbon content is consistent with our earlier estimate of predicted enhancement for these electrodes.

The noise of the HC electrodes was dominated by flow noise (Table I) for all compositions investigated. Consequently, the S/N ratio exhibited much less dependence on composition than did the other series of electrodes (Fig. 2). Scanning electron microscopy and chronoamperometry indicate that the average active and inactive site dimensions of the HC electrodes are five to ten times smaller than those of the 3M-A or 3M-B electrodes (22), reflected in the enhanced signal of the HC electrodes compared with the 3M-B electrodes (Table I). The smaller and more closely spaced active sites result in an apparent electrode area which, on the detector time scale, more closely approaches the geometric area (22), resulting in the larger signal, but also rendering the electrode more susceptible to the effects of flow fluctuations. In the absence of flow fluctuations, it would be reasonable to expect the HC electrodes to exhibit random noise similar to that of the 3M-B electrodes

(equal active areas) and, thus, exhibit a greater S/N ratio than observed with the 3M-B electrodes.

The foregoing discussion suggests the possibility of tailoring a composite electrode for a particular flow detector application so as to maximize the S/N ratio. For applications involving pulsation-free flow, an electrode similar to the 15% HC electrode (consisting of small, closely spaced microelectrodes) is predicted to result in the highest S/N. For chromatographic applications in which flow fluctuations are typically present, a 10-15% 3M electrode (consisting of somewhat larger, more widely spaced microelectrodes) exhibits better flow noise immunity and yields the highest S/N. As observed with continuous electrodes (17), reducing the geometric area of the composite electrode exposed in the flow channel can lead to further improvement in the S/N (3M-B vs. 3M-A electrodes, Fig. 2).

Though similar results could be obtained by tailoring the diameter and spacing of carbon fibers in an array electrode (26), the composite electrodes are considerably simpler to fabricate (19,22). For example, the detection limit for dopamine extrapolated from the results of Wightman et al. (26) for the carbon fiber array electrode (ca. 12 pg versus ca. 50 pg on glassy carbon, S/N = 2 at 1 V vs. SCE) is comparable to the detection limits reported for other phenols (ca. 3-14 pg) on a 15% 3M Kelgraf electrode (5). However, the carbon fiber array required over ten hours to fabricate compared to ca. one hour for a Kelgraf electrode. The more precise control of the size and placement of the microelectrodes in the carbon fiber array would certainly be an advantage for comparing experimental results with theoretical predictions of models describing convective-diffusion at ensembles of microelectrodes.

Finally, we have observed that the composition of a Kelgraf electrode has a rather profound effect on the ability of the electrode to resist fouling. With 5% 3M-B and 10% HC electrodes, the signal observed for repetitive 20 μL injections of 100 μM resorcinol (notorious for fouling electrodes) decreased with each injection such that after 50 injections the signal had decreased by 50%. Resurfacing these electrodes restored the original sensitivity. However, with 15% 3M-B and 20% HC electrodes, the signal from repetitive injections did

not decrease, and 100 injections of 100 μM resorcinol on these two electrodes yielded peak heights with a standard deviation of 2-3%. Indeed, we have used a 15% 3M-A electrode routinely for phenol determinations for over six months without resurfacing or deterioration of response (5). The reason for this composition dependence of electrode fouling is not yet clear. Perhaps it is related to the overall wetability of the composite which increases with increasing carbon content (31). With smaller microelectrodes (lower %C), the binder (Kel-F) surrounding each microelectrode may have a more pronounced influence on the nominal polarity compatibility of solutes and solvent with the microelectrode which in turn influences the tendency of products of the electrode reaction to adsorb onto the surface. Whatever the reason, adjusting the composition of composite electrodes for optimum performance should include consideration of fouling tendencies. It is convenient that the 15% 3M electrodes which display nearly optimum S/N behavior for LCEC applications also exhibit excellent resistance to fouling.

Since double layer charging current is a function of active area while Faradaic current is a function of apparent area (22), a composite electrode may possess an enhanced Faradaic current-to-charging current ratio (compared to a continuous electrode) in detector schemes involving pulsing of the electrode potential. Efforts are continuing in our laboratory to explore and exploit this and other possible advantages of composite electrodes as applied to LCEC.

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REFERENCES

1. Kissinger, P.T., Refshauge, C., Dreiling, R. and Adams, R.N., Anal. Lett. 6, 465, 1973.

2. Bollet, C., Oliva, P. and Caude, M., J. Chromatogr. 149, 625, 1978.

3. Armentrout, D.N., McLean, J.D. and Long, M.W., Anal. Chem. 51, 1039, 1979.

4. Strohl, A.N. and Curran, D.J., Anal. Chem. 51, 1050, 1979.

5. Weisshaar, D.E., Tallman, D.E. and Anderson, J.L., Anal. Chem. 53, 1809, 1981.

6. Takata, Y. and Muto, G., Anal. Chem. 45, 1864, 1973.

7. Lankelma, J. and Poppe, H., J. Chromatogr. 125, 375, 1976.

8. Wightman, R.M., Paik, E.C., Borman, S. and Dayton, M.A., Anal. Chem. 50, 1410, 1978.

9. Hepler, B.R., Weber, S.G. and Purdy, W.C., Anal. Chim. Acta 41, 102, 1978.

10. Strohl, A.N. and Curran, D.J., Anal. Chem. 51, 1045, 1979.

11. Blaedel, W.J. and Wang, J., Anal. Chem. 51, 799, 1979.

12. Girard, J.E., Anal. Chem. 51, 836, 1979.

13. Blaedel, W.J. and Strohl, J.H., Anal. Chem. 36, 1245, 1964.

14. Pungor, E. and Szepesvary, E., Anal. Chim. Acta 43, 289, 1968.

15. Nagy, G., Feher, Zs. and Pungor, E., Anal. Chim. Acta 52, 47, 1970.

16. Fenn, R.J., Siggia, S. and Curran, D.J., Anal. Chem. 50, 1067, 1978.

17. Weber, S.G. and Purdy, W.C., Anal. Chim. Acta 100, 531, 1978.

18. Klatt, L.N., Connell, D.R., Adams, R.E., Honigberg, I.L. and Price, J.C., Anal. Chem. 47, 2470, 1975.

19. Anderson, J.E., Tallman, D.E., Chesney, D.J. and Anderson, J.L., Anal. Chem. 50, 1051, 1978.

20. Chesney, D.J., Anderson, J.L., Weisshaar, D.E. and Tallman, D.E., Anal. Chim. Acta 124, 321, 1981.

21. Anderson, J.L., Weisshaar, D.E. and Tallman, D.E., Anal. Chem. 53, 906, 1981.

22. Weisshaar, D.E. and Tallman, D.E., Anal. Chem. 55, 1146, 1983.

23. King, W.P., Joseph, K.T. and Kissinger, P.T., J. Assoc. Off. Anal. Chem. 63, 137, 1980.

24. Swartzfager, D.G., Anal. Chem. 48, 2189, 1976.

25. Dayton, M.A., Brown, J.C., Stutts, K.J. and Wightman, R.M., Anal. Chem. 52, 946, 1980.

26. Caudill, W.L., Howell, J.O. and Wightman, R.M., Anal. Chem. 54, 2532, 1982.

27. Gueshi, T., Tokuda, K. and Matsuda, H., J. Electroanal. Chem. 89, 247, 1978.

28. Rice, M.E., Galus, Z. and Adams, R.N., J. Electroanal. Chem. 143, 89, 1983.

29. Weisshaar, D.E., Ph.D. Dissertation, North Dakota State University, 1982.

30. Weber, S.G., "The Signal-to-Noise Ratio Problem in Electrochemical Detectors Used in Liquid Chromatography", Presented at FACSS, 1982, Philadelphia, PA.

31. Anderson, J.E., Ph.D. Dissertation, North Dakota State University, 1979.