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SIGNAL STABILITY OF NAFION-COATED THIN MERCURY FILM ELECTRODES FOR STRIPPING VOLTAMMETRY

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Summary—The signal stability of the Nafion-coated thin mercury film electrode (NCTMFE) was studied by using cadmium and lead as test analytes and differential pulse anodic stripping voltammetry as detection method In particular, the effect of the casting solvent and the curing procedure employed in the preparation of the polymer film was examined Best results were obtained with *N,N*-dimethylacetamide as casting solvent and a two-step curing procedure in which the polymer was evaporated to dryness at 55° and cured at 105° with a hot-air gun. Mercury plating was performed *ex situ* An NCTMFE prepared in this manner has a better signal stability than *ex situ*-plated as well as *in situ*-plated conventional mercury film electrodes

The Nafion-coated thin mercury film electrode (NCTMFE) has proved to be very useful in electrochemical stripping analysis. In comparison with the conventional thin mercury film electrode (TMFE), the modified electrode offers enhanced sensitivity when used in conjunction with differential stripping techniques,[1–3] and the anti-fouling properties of the membrane coating make possible the determination of trace metals in difficult matrices such as body fluids without prior digestion of the sample.[4] The preparation of the modified electrode is convenient and rapid,[1] but it invariably adds a step to the overall analytical procedure. This consideration is particularly important in view of the fact that an NCTMFE slowly loses sensitivity and becomes passivated during prolonged use (like any other voltammetric electrode with a surface that is not automatically renewed), and it therefore requires periodic regeneration. Other things being equal, the signal stability and lifetime of the electrode are therefore more important factors for the NCTMFE than for the TMFE. The importance of the signal stability is further emphasized by the fact that a chemical sensor with a monotonically drifting response will introduce systematic errors in quantitative analysis unless calibration and the measurement in the sample take place simultaneously. This requirement is met only in the method of internal standards.

In the present work, the signal stability of the NCTMFE has been examined. More specifically, the peak currents of cadmium and lead measured by differential pulse anodic stripping voltammetry (DPASV) were recorded during repeated stripping experiments We have also investigated whether the signal stability is influenced by the choice of the casting solvent and the curing conditions employed in the preparation of the Nafion film. The selection of casting solvents to be included in the study was guided by previous work which showed that solvents containing the *N,N*-dialkylamide group are capable of dissolving Nafion (with equivalent weight 1100) at the boiling point of the solvent at atmospheric pressure.[5–6] For example, it was shown that Nafion can be dissolved in *N,N*-dimethylformamide (DMF) at a temperature as low as 153° (Ref. 5), although no data are given on the concentration of the resulting Nafion solution after removal of undissolved residues. Likewise, Weber *et al.*[6] succeeded in dissolving Nafion in boiling *N,N*-dimethylacetamide (DMAA) at 165°, which produced a solution containing 0.5% (w/v) of dissolved Nafion. Solvents capable of dissolving Nafion probably act as plasticizing agents, increasing the mobility of the fluorocarbon chain material and promoting the dissolution of the crystalline regions of the polymer.[7–8] The quality of Nafion films cast from solution is related to

the re-formation of the crystalline phase.[7-8] It is therefore likely that solvents suitable for the dissolution of Nafion are also good casting solvents in the preparation of Nafion films. Indeed, it has been shown that durable Nafion films are obtained by evaporation from DMF,[4] but no systematic study of the effect of the casting solvent on the properties of the recast film has been undertaken. Owing to the high sensitivity of the NCTMFE when used in conjunction with DPASV,[1-3] the stability of the signal is a more important criterion for the quality of the modified electrode than is the magnitude of the signal.

EXPERIMENTAL

Apparatus

Voltammetric measurements were performed with a programmable electrochemical analyser.[9] The electrochemical cell comprised a Metrohm 628-50 rotating disk electrode unit with a 3-mm diameter glassy carbon electrode. The reference electrode was a Radiometer K401 saturated calomel electrode (SCE), while the counter electrode was a glass-fitted platinum wire (1 cm long, 0.5 mm thick).

Reagents

Buffers and supporting electrolyte media were prepared from Merck Suprapur reagents and triply distilled water, while other reagents were of analytical grade. A 5% (w/w) solution of Nafion 117 (1100 equiv. weight) in lower aliphatic alcohols and water was obtained from Aldrich. Solutions containing 0.4% (w/w) and 0.2% (w/w) Nafion were prepared by dilution of the stock solution with absolute ethanol. Dilution with water should be avoided as it may cause coagulation of the polymer solution.[10] *N,N*-dimethylformamide (DMF, b.p. 153°), *N,N*-dimethylacetamide (DMAA, b.p. 165°), *N,N*-dimethylpropionamide (DMPA, b.p. 174°), *N,N*-diethylacetamide (DEAA, b.p. 186°) and *N,N*-diethylpropionamide (DEPA, b.p. 191°) were also obtained from Aldrich. The

Table 1 Effects of casting solvent and curing conditions on the stability of DPASV signals obtained with NCTMFE*

	Cd		Pb	
Electrode preparation	Mean change of peak current† (%)	Standard deviation of change of peak current (%)	Mean change of peak current† (%)	Standard deviation of change of peak current (%)
Conventional TMFE, *ex situ* Hg plating	−13	8	−17	6
Conventional TMFE, *in situ* Hg plating	+3	5	−26	6
DMAA + Nafion cured with heat gun	−3	4	+5	4
DMAA + Nafion cured in oven	−2	8	+8	6
DMAA + Nafion (low-thickness) cured with heat gun	−11	6	−12	11
DMF + Nafion cured with heat gun	−6	8	−6	11
DMF + Nafion cured in oven	−14	14	−16	14
DMPA + Nafion cured with heat gun	−6	10	−8	10
DEAA + Nafion cured with heat gun	−29	9	−30	8
DEAA + Nafion cured in oven	−25	7	−14	5
DEPA + Nafion cured with heat gun	−32	9	−28	17
DEPA + Nafion cured in oven	−23	10	−15	7

*All values quoted are calculated on the basis of five separate stability experiments, each commencing with a freshly prepared working electrode. Twenty consecutive signals were acquired during 72 min.

†Change of the DPASV peak current between first and 20th signal

Table 2 Effects of casting solvent and curing conditions on the DPASV peak current*

Electrode preparation	Cd		Pb	
	Mean peak current†	RSD of peak current (%)	Mean peak current†	RSD of peak current (%)
Conventional TMFE, *ex situ* Hg plating	1 0	25	1.0	15
Conventional TMFE, *in situ* Hg plating	1 3	5	0 7	21
DMAA + Nafion cured with heat gun	1.8	13	1.3	21
DMAA + Nafion cured in oven	1.6	12	1 5	17
DMAA + Nafion (low thickness) cured in oven	1.6	11	1 3	17
DMF + Nafion cured with heat gun	1 8	12	1 2	20
DMF + Nafion cured in oven	1.6	16	1 6	13
DMPA + Nafion cured with heat gun	1 9	20	2 5	15
DEAA + Nafion cured with heat gun	1 3	12	1 1	23
DEAA + Nafion cured in oven	2 0	16	0 9	29
DEPA + Nafion cured with heat gun	1.4	9	1 2	12
DEPA + Nafion cured in oven	1 9	18	0 9	25

*All values quoted are calculated on the basis of five separate preparations of the electrode
†The peak currents are given relative to those obtained at the *ex situ*-plated TMFE

0.1M acetate buffer (pH 4.7) employed in the electrochemical studies was prepared from sodium acetate and nitric acid.

Procedure for preparation of NCTMFE

Prior to coating, the glassy carbon electrode was polished with 0.25 μm diamond paste, rinsed with ethanol and dried with lens paper. Coating was done by applying 1 μl Nafion solution and 1 μl casting solvent. Unless stated otherwise the 0.4% (w/w) Nafion solution was employed; coatings prepared from the 0.2% (w/w) Nafion solution are referred to as low-thickness. An open tube, 1 cm longer than the electrode tip, was placed around it and the solvents were evaporated in warm (55°) air stream from a hot-air gun impinging horizontally on the tube. The electrode was rotated slowly during the evaporation step. Subsequently, the polymer was cured in a hot air stream (105°) by holding the hot-air gun (operated at maximum power) immediately above the electrode surface. Alternatively, the polymer film was cured by placing the electrode tip in an oven at 140° for 20 min. Curing at higher temperatures was not attempted owing to the risk of damaging the electrode tip. Mercury was deposited on the glassy carbon/Nafion substrate by electrolysis for 10 min at -1 V *vs* SCE in deaerated acetate buffer containing $2.5 \times 10^{-5}M$ mercury(II). Conventional TMFEs were prepared in the same manner as the NCTMFE apart from the Nafion coating.

Procedure for DPASV measurements

All measurements were performed in 0.1M acetate buffer spiked with $2.0 \times 10^{-7}M$ Cd(II) and $2.0 \times 10^{-7}M$ Pb(II). This solution was also spiked with $2.5 \times 10^{-5}M$ mercury(II) in the experiments with the *in situ*-plated TMFE. Solutions were deaerated with argon for 5 min prior to DPASV measurement. The working electrode was rotated at 750 rpm during deposition, while stripping was carried out in a quiescent solution following a 15 sec rest period. The stripping signals were recorded in differential pulse mode with the following instrumental settings: deposition potential, -1000 mV *vs* SCE; deposition time, 2 min; scan range, -1000 to -50 mV *vs* SCE; pulse height, 50 mV; pulse width, 22 msec; sampling time, 2 msec; pulse repetition time, 0.24 sec; effective scan rate, 12.3 mV/sec. Signals were smoothed with a seven-point Savitsky–Golay algorithm, and the back-

ground signal was corrected for by subtraction of an interpolated linear baseline. A freshly prepared NCTMFE or TMFE was preconditioned by performing two deposition/stripping cycles in the acetate buffer. In the stability studies, the repeated DPASV experiments were performed automatically under computer control

RESULTS AND DISCUSSION

The results of the study of the stability of DPASV signals obtained with the NCTMFE are summarized in Table 1. Data from analogous measurements using a conventional TMFE are also included. Ideally, conclusions about correlations between the manner of electrode preparation and the resulting signal stability should be based on statistical tests. However, an exact statistical treatment of the material is not possible because the true distribution of the measured signal stabilities is not known owing to the relatively smaller number of replicate experiments. As an approximation, statistical testing has been performed by assuming that the t-distribution can be applied and that the standard deviations of the data sets being compared are not significantly different.

The best signal stability is obtained with a NCTMFE cast from DMAA and cured with the hot-air gun Moreover, the variability of the signal stability between individual electrode coatings prepared in this manner is very low Nafion films cast from DMF and cured with the hot-air gun also give a high signal stability, although the reproducibility of the signal stability is poorer than that obtained with DMAA as casting solvent. The difference between the signal stabilities of the NCTMFEs cast from DMAA and DMF and cured with the hot-air gun is not statistically significant. Oven curing of the Nafion films cast from DMAA or DMF does not lead to improvements either in the signal stability or in the reproducibility hereof This finding is surprising as it has been shown[11] that the restoration of the attractive properties of bulk Nafion membranes (*e.g.* mechanical strength, elasticity and insolubility in polar solvents) in the recast film is generally enhanced by an increase in the curing temperature. With DMF as casting solvent, a curing temperature of 140° is sufficient to produce recast Nafion films with properties very similar to those of the bulk material.[11] No corresponding data are available for DMAA. Most probably, the inferiority of the oven curing procedure is due to a rapid and quantitative evaporation of the casting solvent from the thin Nafion film when it is exposed to the curing temperature. Consequently, the casting solvent does not have sufficient time to exert its plasticizing effect on the polymer, which is therefore not properly rearranged into the morphology of bulk Nafion. This hypothesis is supported by the observation that the oven curing procedure yielded better signal stability than the hot-air gun curing when casting solvents with higher boiling points than those of DMF and DMAA were used (see below). From a practical viewpoint, it is doubly advantageous that the best signal stability is obtained by curing with the hot-air gun in the cases of DMF and DMAA, as this procedure is much faster than oven curing.

Initially, a number of NCTMFEs were prepared without any heat treatment of the polymer. The Nafion solution and the casting solvent (DMF or DMAA) applied to the electrode tip were simply allowed to evaporate by standing overnight at room temperature. However, the stability of the DPASV signals of cadmium and lead obtained with this electrode preparation procedure was poor. This result emphasizes the importance of curing the Nafion film at high temperature.

Casting the Nafion film from DMPA also produced a high signal stability, although the variability was higher than in the case of DMAA. However, NCTMFEs cast from DMPA produced very high lead peaks (see below), and this solvent may therefore also be useful. Nafion films cast from DEAA and DEPA and cured with the hot-air gun exhibited poor signal stability. With these solvents, treatment of the polymer in the oven led to some improvement of the signal stability, but it was still inferior to that obtained with DMAA as casting solvent. The difference between the signal stability of the NCTMFE prepared with DMAA and cured with the hot-air gun and the stabilities of the NCTMFEs prepared with DEAA or DEPA and cured in the oven is statistically significant at a 95% confidence level for cadmium as well as lead. DEAA and DMPA are the highest-boiling solvents used in the present study, and the temperatures employed in the heat treatment procedures are probably too low to effect a complete curing of the recast Nafion film. Moore and Martin[11] have demonstrated a positive correlation between the minimum curing temperature needed for full reconstitution of the properties of bulk Nafion

in the recast film and the boiling point of the casting solvent, although other properties of the solvent also play a role.

As can be seen from Table 1, the NCTMFE cast from DMAA and cured with the hot-air gun has better signal stability than the conventional *ex situ*-plated TMFE. The difference in the signal stability of the two electrodes is significant at a 95% confidence level for cadmium as well as lead. This result is highly encouraging, and shows that the NCTMFE has other advantages in addition to its ability to suppress interference from surface-active compounds.[1] The improvement in signal stability at the NCTMFE in comparison with the conventional TMFE can be explained by a mechanical stabilization of the mercury phase by the polymer matrix. The mercury 'film' on the TMFE consists of droplets[12] that can move on the glassy carbon substrate, and morphological changes of the mercury phase such as coalescence or dislodgement of the droplets will therefore take place during use of the electrode. These processes will be suppressed at the NCTMFE owing to the immobilization of the mercury droplets in the polymer matrix.[1] The hypothesis is supported by the fact that poorer signal stability was observed at the low-thickness NCTMFE (cf. Table 1). The *in situ*-plated TMFE yielded a high signal stability for cadmium, while a substantial and reproducible decrease in the lead peak current was observed. Thus, the NCTMFE cast from DMAA and cured with the hot-air gun also compares favourably with this electrode system. The mercury phase on the *in situ*-plated TMFE grows continuously during the repetitive DPASV measurements. However, it is difficult to explain why this process affects the DPASV response of cadmium and lead in different ways. Both metals are highly soluble in mercury and behave reversibly at a mercury electrode, and their diffusion coefficients in mercury are almost identical.[13] Theory predicts[14] that the DPASV peak current of a metal with reversible electrode kinetics is independent of the thickness of the mercury film as long as the diffusion layer in the mercury phase extends throughout the film. This result accords with the observed constancy of the cadmium peak current.

Table 2 summarizes the DPASV peak currents of cadmium and lead obtained with the various preparations of the NCTMFE. Generally, an enhancement of the peak current for both metals is achieved with the NCTMFE in comparison with the *ex situ*-plated TMFE, in agreement with previous results.[1-3] On average, the signal enhancement factor for cadmium is larger than for lead. There does not seem to be any clear correlation between the manner of preparation of the NCTMFE and the DPASV peak currents. A notable exception, however, is the NCTMFE cast from DMPA, which consistently yielded a very high lead signal. This phenomenon is being studied further at present.

In conclusion, a high signal stability of the NCTMFE can be attained by appropriate choice of casting solvent and curing conditions, which attests to the utility of the electrode for practical analysis. Further improvements in the procedure for preparation of the NCTMFE would be greatly facilitated by a more detailed understanding of the processes taking place during the curing of the polymer and by microscopy studies of the modified electrode.

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