THE INFLUENCE OF LEAD UNDERPOTENTIAL DEPOSITION ON THE CAPACITANCE OF THE SILVER–AQUEOUS INTERFACE

JOSEPH T. HUPP, D. LARKIN *,**, H.Y. LIU and MICHAEL J. WEAVER **

Department of Chemistry, Michigan State University, East Lansing, MI 48824 (U.S.A.)

(Received 14th April 1981; in revised form 15th July 1981)

ABSTRACT

The differential capacitance of electrodes formed by the underpotential deposition of lead at a polycrystalline silver substrate in contact with aqueous sodium perchlorate media has been studied in order to assess the influence of the surface atomic layer of the electrode in comparison with that of the underlying bulk metal. A novel method for preparing such surfaces using very dilute lead solutions and a rotating disk electrode was developed whereby the coverage of the resulting lead layers remained constant *in situ* over a wide potential range for long time periods in quiescent solution. It was found that lead layers on silver having coverages in the vicinity of a monolayer and beyond exhibited double-layer properties that were very similar to those for polycrystalline lead electrodes, and markedly different to those for clean silver. This suggests that the surface atomic layer provides the predominant influence upon the double-layer structure. The virtues of employing underpotential-deposited metal films in exploring the influences of the metal surface upon the interfacial structure are pointed out.

INTRODUCTION

The chemical composition of the metal substrate is known to play an important role in determining the thermodynamic properties of metal–electrolyte interfaces, as shown by the large changes in double-layer capacitance and the potential of zero charge (pzc) that are generally observed when the electrode material is altered [1]. At least under conditions where the extent of ionic specific adsorption is small, the variations have been attributed to a combination of the electronic properties of the metal (work function) together with differences in the orientation of solvent dipoles in the inner-layer region [1]. A difficulty in comparing the experimental data obtained to date is that the substitution of one pure metal substrate for another represents a fairly drastic change in system state.

A method of varying the metallic composition of an electrode surface in a more subtle manner is to deposit varying quantities of one metal on to a different metal substrate. A number of systems of this type involve "underpotential deposition"

---

* Permanent address: Department of Chemistry, Towson State University, Towson, MD 21204, U.S.A.
** Authors to whom correspondence should be addressed.

(upd) of the metal in submonolayer amounts [2]; this facilitates the preparation of surfaces *in situ* whose composition can be varied in a systematic and controllable way from the pure substrate through to a monolayer of deposited metal and beyond. In particular, the comparison of the double-layer properties of the pure substrate with those for surfaces having monolayer and multilayer quantities of the depositing metal should enable an assessment to be made of the relative structural influences of the surface atomic layer and the underlying bulk metal.

Nevertheless, to our knowledge, there are no reports of the determination of the double-layer capacitance at electrodes containing such upd layers. We have recently been investigating the kinetics of simple inorganic electrode reactions at various metal surfaces in order to explore the possible influences of the electrode material upon the reaction energetics. In conjunction with these studies, we have obtained double-layer structural data at polycrystalline silver and lead electrodes in a variety of aqueous electrolytes, including adsorption data for a number of anions and transition–metal complexes [3,4]. It has been shown that lead forms stable upd layers on a silver substrate; the conditions necessary for their formation and some properties of these layers are well established [2,5–7]. We have therefore chosen to study the double-layer capacitance of electrode surfaces formed by the deposition of varying amounts of lead on a silver substrate in aqueous sodium perchlorate media. This electrolyte was chosen in view of the likelihood that perchlorate anions are only weakly adsorbed, at least at potentials in the vicinity, and negative, of the pzc. (Concentrated fluoride electrolytes could not be employed owing to the insolubility of lead fluoride.) Capacitance–potential plots were determined for lead layers with coverages both below and above monolayer levels. These results are presented in the present communication. A comparison of the extent of thiocyanate specific adsorption at bulk lead and upd lead/silver surfaces is also given.

EXPERIMENTAL

All solutions were prepared and all recrystallizations performed using water which was first distilled from alkaline permanganate and then subsequently distilled from a quartz non-boiling still (Model PB2, Dida-Sciences, Montreal). Analytical grade reagents were generally used. A stock solution of sodium perchlorate was prepared by neutralizing sodium carbonate with 70% perchloric acid, then heated and filtered. Solid sodium perchlorate, used to prepare all solutions for electrochemical studies, was obtained by double recrystallization from this stock solution. Sodium thiocyanate was twice recrystallized from water before use. Differential capacitance curves measured at a hanging mercury drop electrode in solutions prepared from these reagents were stable for at least several hours and conformed to literature values.

The electrochemical cell was of all glass construction and consisted of two compartments separated by a fine glass frit. One compartment contained the counter and working electrodes, the other the reference electrode. The counter electrode was a platinum spiral which was mounted centrally about the working electrode. The

bulk silver and lead working electrodes were of a rotating disk construction, consisting of a silver or lead disk (geometrical surface area of 0.0491 and 0.105 cm^2 respectively), sheathed in Teflon and connected to a steel shaft. A commercial saturated calomel electrode (SCE) filled with saturated NaCl rather than KCl was used as the reference electrode. All solutions were deoxygenated using nitrogen, which could be bubbled through the cell solution or passed over the solution surface. Residual traces of oxygen were removed by first passing the nitrogen through a column packed with BASF R3-11 catalyst heated to 140°C. All glassware was soaked in a 1:1 nitric/sulfuric acid mixture for 24 h, then soaked in water at least one day and dried in an oven at 150°C before use.

Electrode preparation and capacitance measurements

The silver substrate electrode was pretreated using an electropolishing procedure which was a modified version of that given in refs. 8 and 9; it is described in detail elsewhere [3]. The bulk lead electrode was prepared by mechanical polishing on a wheel (Buehler), using alumina (Linde, Buehler) of decreasing grit size down to 1.0 μm. It was rapidly washed and transferred to the cell solution (0.5 M NaClO$_4$) in order to minimize air oxidation, and held at -1.5 V prior to use [4]. Lead electrodes were also prepared using a chemical polishing technique [10] which yielded very similar capacitance–potential curves as those obtained following mechanical polishing. However, the latter method was performed for most work since it resulted in more stable and reproducible surfaces [4].

The upd lead electrodes were prepared using the following novel procedure. The pretreated silver electrode was attached to a rotating disk electrode assembly (Model ASR2 rotator, Pine Instruments), then introduced into the cell containing the appropriate electrolyte and the differential capacitance C determined as a function of electrode potential E. Sufficient acidic lead fluoride solution was then added to bring the lead concentration in the cell to between 0.2 and 0.6μM. (The solutions were made slightly acidic, pH ~ 3.5, to minimize adsorption of lead onto the glass cell walls [11].) The electrode potential was then set such that it was negative of the value required for upd but positive of that required for bulk lead deposition. (The exact potentials used were of course dependent on the lead ion concentration in solution.) The rotator was then turned on (a rotation speed of 600 rpm being used in all experiments) and the electrode held at the preset potential for a known time (*ca.* 10 min). At the end of this period the deposited lead was stripped off using an anodic linear potential sweep and the current–potential profile recorded. A P.A.R. Model 174A polarographic analyzer coupled with a Houston Model 2000 X–Y recorder were employed for this purpose. The procedure was repeated using gradually longer formation times until a upd monolayer was deposited. This point was determined as that beyond which the size of the anodic stripping peak no longer increased with time. A typical stripping curve is shown in Fig. 1 (curve a).

It was desired to determine the differential capacitance C of the upd layer over as wide a range of electrode potential E as possible at a series of *constant* lead
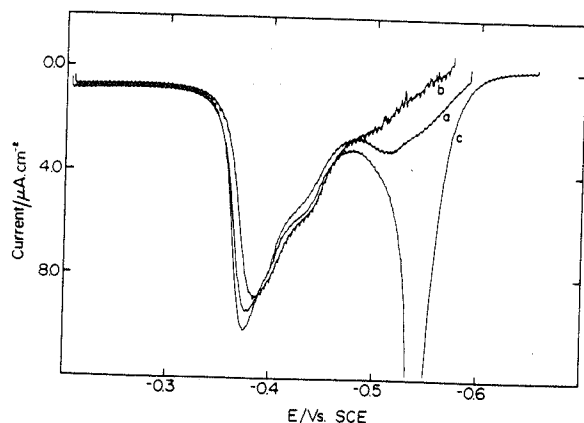
302

Fig. 1. Linear sweep current–potential curves for anodic removal of lead layer deposited on silver. Sweep rate 5 mV s^{-1}, electrode rotated at 600 rpm. Electrolyte was 0.5 M NaClO$_4$ adjusted to pH 3.5 with HClO$_4$, containing 0.6 μM Pb^{2+}. Lead deposits corresponding to anodic stripping curves (a)–(c) formed as follows: (a) electrode rotated at 600 rpm, held at -0.585 V for 10 min; (b) as (a) but held at -1.20 V for additional 20 min with no rotation; (c) electrode rotated at 600 rpm, held at -0.65 V for 10 min.

coverages. Therefore, it was necessary for the layer, once formed, to be stable over the period of time (*ca.* 20 min) required to obtain a complete set of C vs. E measurements for a particular electrode and solution composition. Initially, attempts were made to avoid further deposition of lead by transferring the electrode to another solution free of Pb^{2+}. This method was only partly successful. However, it was subsequently discovered that provided that only very small ($<1\ \mu M$) bulk concentrations of Pb^{2+} were employed to form the upd layers, no further significant lead deposition occurred during the time required to perform the capacitance measurements if the electrode rotator was turned off and the solution unstirred. This was true even at potentials sufficiently negative so that the deposition of "bulk" lead can occur. A typical result is shown in Fig. 1 (curve b). It is seen that the stripping curves a and b are almost identical, even though the electrode was held at -1.2 V for an additional 20 min without rotation prior to recording the latter curve. In experiments where a monolayer or less of upd lead was formed, the alteration in coverage during the time required to perform the capacitance measurements generally amounted to less than 2–3%. On the other hand, rotation of the electrode allowed the deposition of lead to occur at a controlled rate, even at potentials where bulk lead was deposited. The presence of bulk, in addition to upd, lead deposits were determined from the appearance of a second peak on the anodic stripping curve at potentials less positive than those required for the dissolution of upd lead (curve c in Fig. 1).

The extent of upd and bulk lead deposition was determined individually from the coulombic charge under the stripping curves. The fractional coverage of upd lead was determined from the ratio of the anodic charge required to strip the layer to the

charge required to remove a monolayer. This method involves the assumption that the so-called "electrosorption valency" γ of the deposited lead is independent of the coverage θ. Although this is unlikely to be entirely correct, the error so introduced is unlikely to be major; for upd lead on silver γ has been found to be close to the value (2.0) expected for the electrodeposition of ordinary lead [6].

Differential-capacitance measurements were made using a Wien configuration bridge of in-house design. An ac frequency of 1.0 kHz was normally employed. Alteration of the frequency between 0.5 and 1.5 kHz yielded variations in C of typically less than 10%, the apparent values of C generally increasing with decreasing frequency.

RESULTS

Figure 2 summarizes typical plots of the differential electrode capacitance C against the electrode potential E for polycrystalline silver (curve a), a monolayer of upd lead on silver (curve b), upd lead with additional (ca. two monolayers) bulk
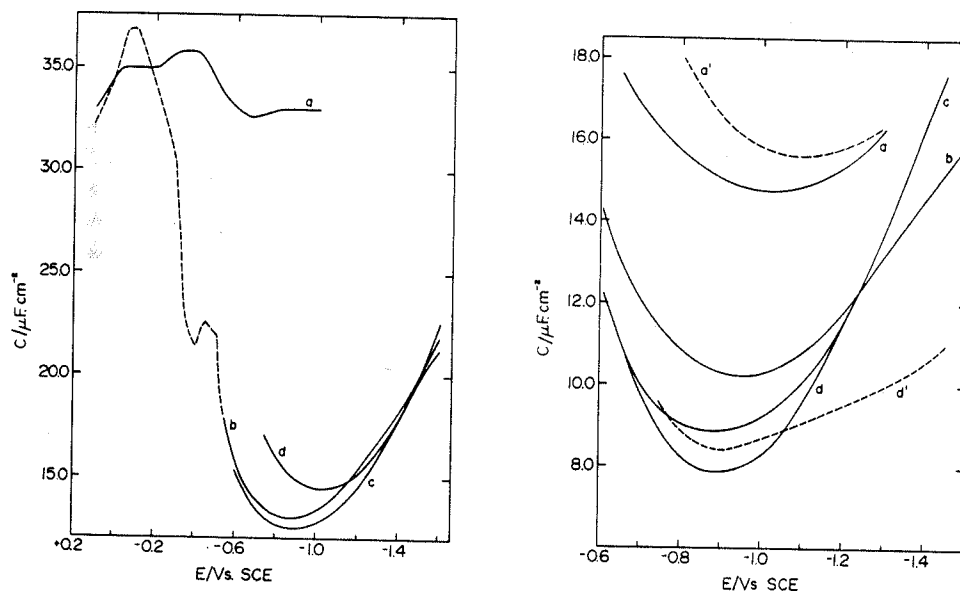

Fig. 2. Differential electrode capacitance C vs. electrode potential E for: (a) polycrystalline silver; (b) silver containing a monolayer of upd lead; (c) as in (b) but with additional ca. 2 monolayers of bulk lead deposit; (d) polycrystalline lead. Lead layer prepared as indicated in caption to Fig. 1 and the text. Electrolyte was 0.5 M NaClO$_4$, pH 3.5; for (b) and (c) additionally contained 0.6 μM Pb^{2+}.

Fig. 3. Differential electrode capacitance C vs. electrode potential E for monolayer upd lead on polycrystalline silver (curves a–d) and polycrystalline lead (curves a′,d′) as a function of ionic strength of sodium perchlorate, adjusted to pH 3.5. Concentrations of NaClO$_4$: (a,a′) 0.5 M; (b) 0.1 M; (c) 0.05 M; (d,d′) 0.01 M.

deposit (curve c) and polycrystalline bulk lead (curve d), each immersed in aqueous 0.5 M sodium perchlorate. This large ionic strength was chosen so to minimize the influence of the diffuse layer. The dashed part of curve b represents the potential region where the upd layer coverage falls progressively below unity as the potential becomes less negative, eventually (at about -0.3 V) being removed entirely. Anodic removal of the lead deposits gave silver surfaces that exhibited $C - E$ curves that were very similar (C within ca. 10%) to those for the original silver surface, indicating that lead deposition did not produce any noticeable irreversible changes in the surface structure.

The dependence of C upon the ionic strength is shown in Fig. 3 for upd lead (curves a–d) and bulk lead (curves a',d'). In each case, there are close similarities between the corresponding C–E curves for upd and bulk lead, the capacitance generally being substantially smaller than for bulk silver. Also, as expected, the deposition of lead beyond a monolayer (i.e. forming "bulk" rather than upd lead layers) yielded C–E curves that are very similar to those for polycrystalline bulk lead (Figs. 1c,d).
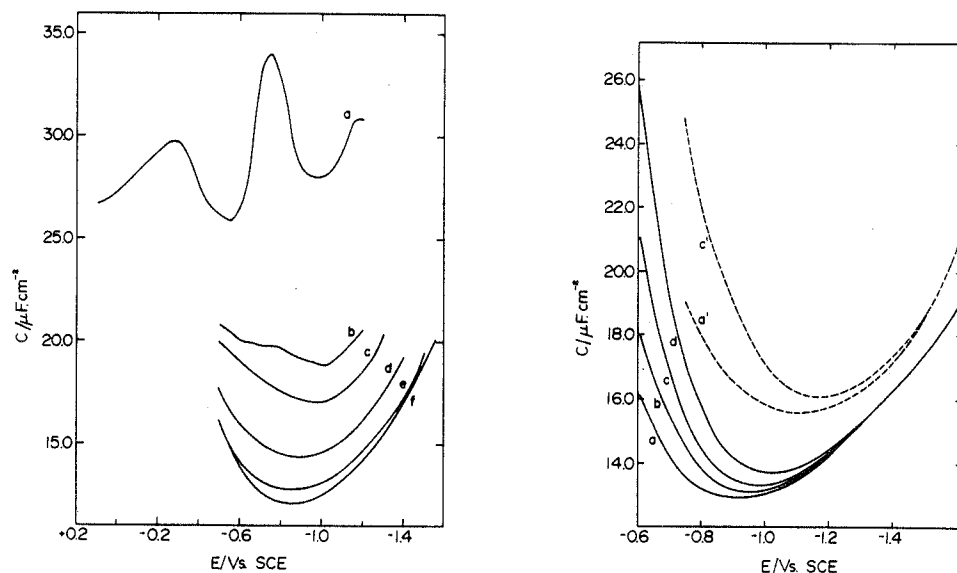

Fig. 4. Differential electrode capacitance C vs. electrode potential E for upd lead layer on polycrystalline silver having various coverages of lead. Electrolyte was 0.5 M NaClO$_4$, pH 3.5, with 0.6 μM Pb^{2+}. Lead coverages (percentage of monolayer): (a) 0%; (b) 22%; (c) 35%; (d) 61%; (e) 93%; (f) 100%.

Fig. 5. Effect of thiocyanate anions upon the differential capacitance–potential curves for a polycrystalline silver electrode covered with monolayer of upd lead (curves a–d), polycrystalline lead electrode (curves a',c') in 0.5 M NaClO$_4$, pH 3.5. NaNCS concentrations: (a,a') zero; (b) 5.8 mM; (c) 24 mM; (d) 82 mM; (c') 27 mM.

The capacitance data for silver are in reasonable agreement with earlier results [12]. The capacitance values for bulk lead are somewhat smaller than obtained earlier [13]; this discrepancy is probably due to differences in the electrolytes and the electrode pretreatment methods employed [4].

The influence of submonolayer upd lead on the $C-E$ curves for a silver substrate in 0.5 M NaClO$_4$ is summarized in Fig. 4. It is seen that capacitance values that are markedly closer to bulk lead than silver are obtained for upd coverages as low as 35%.

Figure 5 contains a comparison of the influence of thiocyanate specific adsorption on the $C-E$ curves at upd lead monolayer and bulk lead electrodes. In both cases the capacitance increased progressively as the thiocyanate concentration was increased and as the potential was made less negative, as expected for simple anion specific adsorption at a constant ionic strength [14]. However, at a given potential the capacitance increases were somewhat larger for bulk compared to upd lead (Fig. 5).

DISCUSSION

Taken together, the results presented in Figs. 2–5 demonstrate that upd lead having coverages in the vicinity of a monolayer and beyond exhibit double-layer properties that are very similar to bulk lead, and very different from those obtained for the silver substrate. Admittedly, some differences are observed: the capacitances tend to be somewhat larger for the bulk lead electrode with a minimum at significantly (ca 0.1 V) more negative potentials, and appear to induce somewhat greater amounts of thiocyanate specific adsorption than the upd lead surface. However, these disparities are relatively minor and may well reflect differences in surface pretreatment rather than inherent structural dissimilarities. The effective pzc of the upd and bulk lead surfaces appears to be quite similar, as shown by the broad minimum at −0.90 V found for both surfaces in dilute perchlorate solutions (Fig. 3).

From these results, the structure of the double layer for these systems, as determined by the electrode capacitance and the pzc, seems to be determined primarily by the composition of the first atomic layer, and is surprisingly insensitive to the nature of the underlying metal substrate. This may occur because the double-layer properties arise chiefly from the interaction between the inner-layer water molecules and the surface metallic layer. Since the electrosorption valency for lead on silver has been found to be close to that expected for bulk lead [6], and the magnitude of the upd effect for the Pb/Ag system is relatively small (0.16 V) [2], it seems plausible that the nature of the water–surface interactions for upd and bulk lead could be similar. It would be most interesting to gather corresponding data for upd systems such as Ag/Au and Pb/Au for which the underpotential effect is larger than for Pb/Ag [2].

Another facet of the present results is that they suggest that a useful way of obtaining comparative double-layer data at different surfaces would be to employ the most noble surface as a substrate upon which the other surfaces to be compared could be formed by electrodeposition. Such an approach avoids the uncertainties

arising from differences in roughness factor, pretreatment, electrode geometry, etc. that are inevitable when double-layer parameters for two different electrode materials are compared. Thus, the data in Fig. 2 clearly indicate that the double-layer capacitances are at least a factor of two smaller at lead than at silver, at least in the potential region (-0.8 V to -1.0 V) where specific ionic adsorption is unlikely to provide a major influence. This difference is not inconsistent with the speculation that the inner-layer capacitance at the pzc for a series of different metals increases as the "degree of hydrophilicity" (i.e. the tendency to orient inner-layer water molecules) increases [1c]. Thus, as the average pzc for polycrystalline silver and lead in perchlorate media are similar [3,4] (ca. -0.9 V vs. SCE), the measured capacitance C at high ionic strengths in the vicinity of -0.9 V may be anticipated to be larger for silver than for lead since the former metal could well be more hydrophilic. Another important factor responsible for the larger capacitance seen at silver may be the relatively small inner-layer thickness due to the location of the water molecules in interstitial lattice sites on the silver surface [15].

One surprising result is the sharp decreases in C seen as the coverage of the upd lead increases (Fig. 4). The simplest model for the double-layer structure under such conditions is one where the regions covered by lead and silver contribute to the overall measured capacitance in proportion to the fraction of the surface occupied by each metal. Clearly, that model is not appropriate to the present system: for example, at only 35% coverage of lead, the measured capacitance had decreased roughly three-quarters of the way between the pure silver and lead monolayer values (Fig. 4). One possible explanation is that the lead is preferentially depositing on one particular crystallographic plane of silver that is chiefly responsible for the larger values of C seen for pure silver, so that coverage of only a fraction of the silver surface by lead atoms would be sufficient to greatly decrease C. However, Valette and Hamelin [16] have found that the capacitance of all three major crystallographic planes of silver exhibit similarly large values of C at high ionic strenths in the potential range of interest here (ca. -0.7 to -1.2 V vs. SCE). Therefore, some lead deposition on all three crystallographic planes of the polycrystalline silver surface would seem to be necessary in order to account fully for the observed decreases in C. A more likely explanation of the results in Fig. 4 is that the deposition of individual lead atoms alters significantly the inner-layer structure for a number of surrounding silver atoms. This appears reasonable in view of the likelihood that each lead atom is deposited into a "pocket" bordered by at least three or four silver atoms, so that the inner-layer structure would probably be altered at each of these nearest-neighbor silver atoms.

On the basis of the present results, double-layer structural studies of upd and related metal layers promise to provide a valuable and novel approach for probing the structural details of metal-electrolyte interfaces. Such surfaces can be formed in a highly controllable manner allowing subtle as well as major changes in the surface metallic composition to be made *in situ*, yielding surfaces of well-defined composition. It would be desirable to extend such measurements to other systems, including single-crystal surfaces. In addition, such upd layers provide a valuable way of

systematically altering the properties of the metal surface for the purpose of examining the details of electrocatalytic phenomena [17]. The acquisition of further double-layer structural data for upd layers, together with parallel kinetic measurements for simple electrode reactions following both inner-sphere and outer-sphere mechanisms are the object of current experiments in our laboratory.

ACKNOWLEDGEMENT

REFERENCES

1 For reviews, see: (a) A.N. Frumkin, O.A. Petrii and B.B. Damaskin in J.O'M. Bockris, B. E. Conway and E. Yeager (Eds.), Comprehensive Treatise of Electrochemistry, Vol. I, Plenum Press, New York, 1980, Ch. 5; (b) S. Trasatti in H. Gerischer and C.W. Tobias (Eds.), Advances in Electrochemistry and Electrochemical Engineering, Wiley, New York, 1977, p. 213; (c) S. Trasatti in B.E. Conway and J.O'M. Bockris (Eds.), Modern Aspects of Electrochemistry, Vol. 13, Plenum Press, New York, 1979, Ch. 2.
2 D.M. Kolb, M. Przasnyski and H. Gerischer, J. Electroanal. Chem., 54 (1974) 25.
3 D. Larkin, K.L. Guyer, J.T. Hupp and M.J. Weaver, submitted for publication.
4 H.Y. Liu, D. Larkin and M.J. Weaver, to be submitted.
5 A. Bewick and B. Thomas, J. Electroanal. Chem., 70 (1976) 239; 84 (1977) 127.
6 H. Bort, K. Jüttner, W.J. Lorenz and E. Schmidt, J. Electroanal. Chem., 90 (1978) 413.
7 M. Bratoeva, Sov. Electrochem., 16 (1980) 19.
8 K.L. Guyer, S.W. Barr, R.J. Cave and M.J. Weaver, in S. Bruckenstein, J.D.E. McIntyre, B. Miller and E. Yeager (Eds.), Proc. 3rd Symp. on Electrode Processes, Electrochemical Society, 1980, p. 390.
9 S.W. Barr, K.L. Guyer and M.J. Weaver, J. Electroanal. Chem., 111 (1980) 41.
10 A. Bewick and J. Robinson, J. Electroanal. Chem., 60 (1975) 163.
11 R. Salin and B.G. Cooksey, J. Electroanal. Chem., 106 (1980) 251.
12 E.S. Sevastyanov, M.N. Terakopyan and V.K. Chubarova, Soc. Electrochem., 16 (1980) 368.
13 V.F. Ivanov and Z.N. Ushakova, Sov. Electrochem., 9 (1973) 753.
14 E. Dutkiewicz and R. Parsons, J. Electroanal. Chem., 11 (1966) 100.
15 G. Valette, J. Electroanal. Chem., 122 (1981) 285.
16 G. Valette and A. Hamelin, J. Electroanal. Chem., 45 (1973) 301.
17 R.R. Adzič, Isr. J. Chem., 18 (1979) 166.