

Properties and Use of a Lead Cathode at Very Negative Potential

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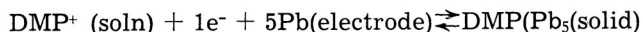
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The properties of lead cathodes at a very negative potential were studied on the basis of recent reports. The effects of the following factors on the »cathodic corrosion« of lead as well as on the preparative reduction of cyclohexanone as a test substance at lead cathode were investigated: the charge, current density, electrolyte composition, kind of the lead foil with respect to lead purity. The results of preparative electroreductions using both mercury and lead cathodes in identical reaction conditions were compared and discussed with regard to more practical aspects of their realization. The relation between the results obtained for the »cathodic corrosion« and for the overall cathode reaction at a lead cathode was also discussed. It was presumed that the overall reduction of cyclohexanone in the reaction conditions described in the paper (constant current density) consisted of two competitive reactions: a minor part of direct electron transfer and a predominant part of an indirect reduction using tetraalkylammonium lead.

INTRODUCTION

It is known¹⁻³ that Pb cathode exhibits certain electrocatalytic properties in nonaqueous medium or with a controlled small amount of water and in the presence of dimethylpyrrolidinium (DMP⁺) ion. Namely, it was found that reduction of DMP⁺ at a Pb cathode leads to an interaction with the metal according to the reaction scheme:



The product of this reaction, the »black powder« DMP(Pb)₅, whose electrogeneration kinetics was also studied,⁴ like DMP(Hg)₅, possesses potentially strong reductive properties, where the regeneration of DMP⁺ and the metal takes place as a result of the oxidation of DMP(Pb)₅. So, in fact, DMP(Pb)₅ acts as an electrocatalyst.

The behaviour mentioned above is not limited to DMP electrolytes. In the presence of tetraalkylammonium (TAA) salts similar reactions were apparent on a Pb cathode and we can presume that compounds with analogous composition R₄N(Pb)₅ are formed. But, here, the term »indirect reduction using tetraalkylammonium lead« instead of »electrocatalytic« seems to be more appropriate because, really, the rate of used lead in this case is higher than »catalytic«.

The main goal of the present work was not to study the mechanism and kinetics of indirect reduction using TAA salts at a lead cathode, but primarily to investigate the still unexplored possibilities of application of the behaviour mentioned above to realize preparative electroreductions, to elucidate the effect of some parameters which may be able to influence and to facilitate these reductions. For this purpose, first the effects of some factors on the amount of »cathodic corrosion« of lead were investigated, such as the kind of solvent and TAA salt, concentration of TAA salt, current density, charge, the kind of Pb material with respect to lead purity *etc.* The term »cathodic corrosion« is common in the literature cited above. The use of quotation marks means that this term should be used with care and also the system might be called, for example, a consumable cathode. In continuation, reduction of a »difficult to reduce« organic compound as cyclohexanone, whose electroreduction at a Hg cathode was described,⁵ was chosen as the test reaction to study the effect of all the factors mentioned above on the results of preparative electroreductions at a Pb cathode. Finally, a comparison was made of the electroreduction results with those obtained using a Hg cathode in order to validate the new procedure, as well as with our own results for the »cathodic corrosion« of lead.

EXPERIMENTAL

Materials

The cathode was a Pb foil (Merck, *p. a.*, 99.99⁰/₀; TOP, min. 99.9⁰/₀). The TAA salts, tetrabutylammonium tetrafluoroborate TBA BF₄ and tetrabutylammonium iodide TBAI, as well as the solvents, DMF and acetonitrile (HPLC grade) were used as purchased from Aldrich. Cyclohexanone was Merck, *p. a.* grade.

Cyclic Voltammetry

Measurements were performed using an Amel 563 Multifunction Unit with Function generator 564, Potentiostat 551 and X—Y Recorder 862/D. The working electrode was a Pb foil (0.126 cm²) purchased from Merck (*p. a.* grade), prepared as described earlier.⁶ The reference electrode was a SCE,⁷ the counter electrode was an Ingold Pt 805NS and the cell was an Amel-Model 494 Universal cell (50 ml).

Preparative Electrolysis

Experiments were carried out at constant current using a Fisher Electro-analyzer with a coulometer. During several experiments, the potential was also determined only at the beginning and at the end of electrolysis using a SCE.⁷ The cathode was a Pb foil (20 cm²) at the bottom of a glass and the counter electrode was a platinum flag (4.5 cm²) enclosed in an alundum cup (Fisher) as the anode compartment. The cell was kept in a thermostat (VEB, Type NBE) or in an ice bath throughout the experiments and nitrogen was bubbled through the catholyte for 10 min prior to and during the experiment.

In a typical experiment, 0.25 ml of cyclohexanone was dissolved in 25 ml of the electrolyte solution and the anolyte (10 ml) consisted of electrolyte solution only. To determine the »cathodic corrosion« of lead (weight loss), the cathodes were washed with water and acetone, dried and weighed before and after electrolysis.

Samples were taken at various electrolysis times and analyzed by means of GC with n-octane as the internal standard. GC analyses were performed with a 3m × 3mm column (3⁰/₀ Carbowax 20M + 3⁰/₀ OV-210 on Supelcoport 80/100) and a Perkin-Elmer GC-900 gas chromatograph with a flame ionization detector. Cyclohexanol, the product of preparative electrolysis of cyclohexanone, was isolated

by extraction with diethylether after the completion of electrolysis and identified by comparison of the IR and ^1H NMR spectra with a sample purchased from Aldrich.

RESULTS AND DISCUSSION

The cyclic voltammogram of the electrolyte solution (0.05 M TBA BF_4 in DMF), presented in Figure 1, curve a, shows the formation of tetrabutylammonium lead starting at approx. -2.7 V *vs.* SCE. Cyclohexanone (0.001 M in the same electrolyte solution) exhibits only a shoulder on rising background current (curve b) but no anodic peak on the reverse scan. The data mentioned above point to a possibility of preparative reduction of cyclohexanone by indirect reduction using tetraalkylammonium lead in competition with a direct electron transfer reduction.

To investigate the effect of several possible factors on the »cathodic corrosion« of lead, we first performed electrolyses without any arganic substrate. The experiments were made at 20°C in the same cell as for preparative electrolyses. The results (the average values of at least three experiments using a new lead cathode in each) are shown in Table I. The

TABLE I
»Cathodic corrosion« of lead cathode, DMF, 20°C , lead 99.99%

	TAA salt	Q/C	Current density	Weight loss
			mA cm^{-2}	mg
1	TBA BF_4	(0.05 M)	72.0	110.0
2	"	"	144.0	212.0
3	"	"	72.0	184.0
4	"	"	144.0	322.5
5	"	(0.1 M)	72.0	131.5
6	"	"	144.0	241.5
7 ^a	"	(0.05 M)	72.0	93.0
8 ^b	"	"	72.0	41.5
9	TBAI	(0.05 M)	72.0	105.0

^a Lead (min. 99.9%) cathode.

^b Acetonitrile instead of DMF.

effects of the following factors were investigated: charge and current density, solvent, kind and concentration of the TAA (TBA) salt, kind of lead foil with respect to lead purity.

During all experiments the formation of a »dark powder« was visible in catholyte as the bulk product as well as at the lead surface. This indicates the »cathodic corrosion« of lead and the formation of TBA $(\text{Pb})_5$ (solid). The values of »weight loss« (Δw) as a measure for the »cathodic corrosion« show that for the same current density corrosion is proportional to charge. With increasing current density the corrosion also increased, but this amount is only about 70% for the double increase of current density from 1.0 to 2.0 mA cm^{-2} . We believe, not going into details, that this is due to the fact that the formation of TBA $(\text{Pb})_5$ normally depends on the potential of a lead cathode (see Figure 1). For the double increase of the TBA BF_4 con-

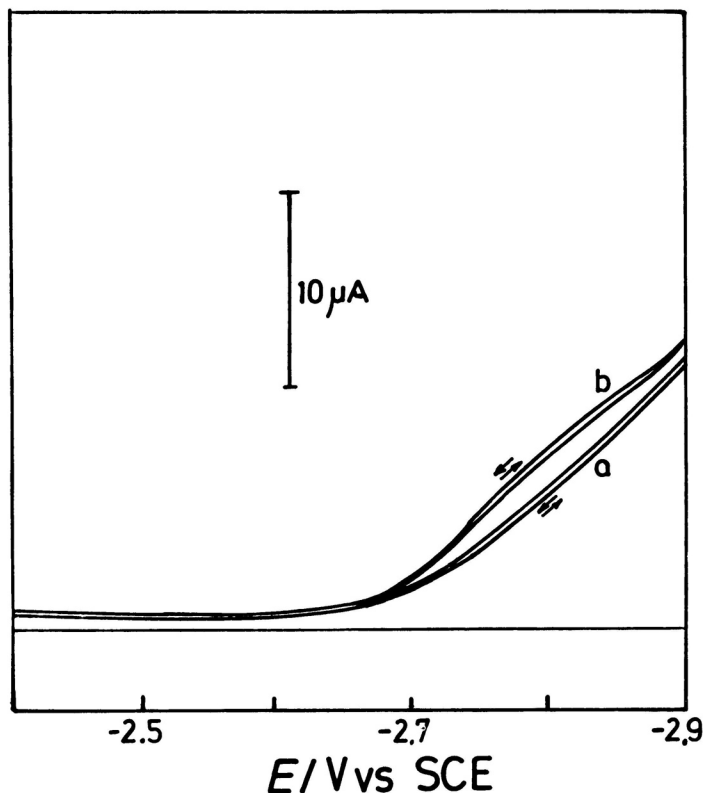


Figure 1. CV for cyclohexanone at Pb cathode, $v = 20 \text{ mV s}^{-1}$;
 (a) electrolyte solution DMF, 0.05 M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$;
 (b) 0.001 M cyclohexanone in (a).

centration from 0.05 M to 0.1 M, the »weight loss« is smaller (only about 20% — entry 5, Table I). The »cathodic corrosion« of lead in acetonitrile is only about 40% of the corrosion in DMF (entry 8). The effect of solvent on the »weight loss« of lead has not been extensively investigated yet. Many parameters can influence, we mention here only the possible effect of small quantities of water, the difference in physical properties of solvents such as conductivity, dielectric constants *etc.* TBAI, which is a significantly cheaper substance than TBA BF_4 , exhibits nearly the same amount of »cathodic corrosion« (entry 9) and, finally, the use of a lead foil with slightly smaller purity but also a much cheaper material showed a decrease in corrosion by about 10% (entry 7).

To investigate to what extent the »cathodic corrosion« corresponds to its »electrocatalytic« activity, we carried out preparative electroreductions of cyclohexanone under similar conditions, investigating the same parameters as described in experiments with »cathodic corrosion«. In comparison, the electroreductions of cyclohexanone using a mercury cathode were also made, reproducing the reaction from literature⁵ in our reaction conditions. This result is given in Table II (entry 1). Electroreductions of cyclohexanone were

also carried out for practical reasons at constant current and the cathode potential was measured only in experiment 2 at the start ($E_{\text{init}} = -2.75$ V vs. SCE) and at the end ($E_{\text{end}} = -2.80$ V vs. SCE) of electroreduction. These experiments were made at 5°C in order to minimize possible undesirable reactions of $\text{TBA}(\text{Pb})_5$ and were generally carried out to complete the conversion of the reactant, *i.e.* until the GC analysis indicated the absence of cyclohexanone in the reaction solution. When electroreductions indicated to be very slow (entries 5—7, Table II), the reactions was stopped at $Q = 5$ F mol $^{-1}$. Cyclohexanol was obtained as the main product of all electroreductions mentioned above. This fact is in accord with the literature data.⁵ It is noteworthy that no amount of possibly formed smaller quantities of »pinacol« during particular preparative experiments could be detected by the described GC method. Also, formation of the »dark powder« was visible in all experiments, but it was not as remarkable as earlier.

TABLE II

Preparative electroreductions of cyclohexanone, DMF, 5 °C, 1.0 mA cm $^{-2}$

	Cathode	TAA salt		Q F mol $^{-1}$	Cyclo- hexanone % ₀	Cyclo- hexanol % ₀
1	Hg	TBAF $_4$	(0.05 M)	2.7	0	76
2	Pb (99.99% ₀)	"	"	4.6	0	71
3 ^a	"	"	"	4.8	0	70
4	"	"	(0.1 M)	4.3	0	67
5	Pb (min. 99.9% ₀)	"	(0.05 M)	5.0	20	53
6 ^b	Pb (99.99% ₀)	"	"	5.0	55	26
7	"	TBAI	"	5.0	50	28

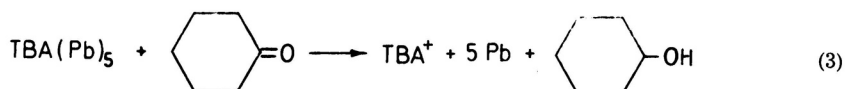
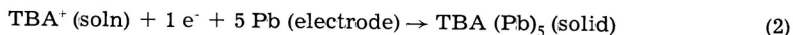
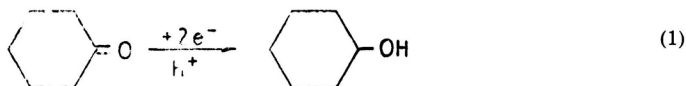
^a Current density 2.0 mA cm $^{-2}$.

^b Acetonitrile instead of DMF.

The yield of cyclohexanol during the electroreduction using a Hg cathode (entry 1, Table II) nearly corresponds to the value cited before.⁵ Using identical conditions at a Pb cathode, the yield was 71%₀ but with smaller current efficiency (entry 2). In general, it may be mentioned that the obtained results predominantly correspond to the data for »cathodic corrosion«. However, there are exceptions. First of all, for example, approximately the same result was obtained with current densities of 1.0 and 2.0 mA cm $^{-2}$ (entry 3). The electroreduction with 0.1 M TBA BF $_4$ did not proceed better than when using a twice smaller concentration of the same salt, so that the latter turned out to be more convenient. Although the »cathodic corrosion« using TBAI was approx. equal to the value obtained using TBA BF $_4$ (Table I), preparative electroreduction of cyclohexanone proceeded slower with TBAI. The reduction using a Pb foil in a smaller quality was also slower (entry 5, Table II), but still sufficient to consider this kind of cheaper material in practice.

It is necessary to mention that, for comparison, the extent of the »cathodic corrosion« of lead during preparative electroreductions of cyclohexanone was also determined (experiment 2, Table II). The average corrosion was by

30—40% smaller than the results given in Table I, entries 1 and 2. This may be explained by the fact that this difference, 30—40%, corresponds to an electron transfer part (reaction 1) in the overall electrode reaction and the rest is the part of an interaction of TBA⁺ with lead followed by an indirect reduction using tetrabutylammonium lead (reactions 2 and 3):



It seems that such a ratio may be expected on the basis of the CV measurements (Figure 1), because the preparative electroreduction started at about -2.75 V vs. SCE . Thus in fact, all discussion mentioned above refers to the effect of investigated parameters on the overall reaction, not only on its part of »indirect reduction using tetraalkylammonium lead«, although the latter predominates in comparison with a part of direct electron transfer reaction. It may also be noted that a repeated experiment of cyclohexanone reductions, using the same lead cathode, did not give a significant decrease of cyclohexanol yield in comparison with the first experiment cited in Table II.

CONCLUSIONS

In general, reaction conditions like those described in our paper are considered in recent literature as competitive with Birch's reductions of »difficult to reduce« organic compounds. Thus, to sum up, we can say that the activity of a lead cathode in an indirect reduction using tetraalkylammonium salts is, in fact, some what smaller in comparison with a mercury cathode, but this activity seems to make it possible for the lead cathode to replace successfully a mercury cathode in preparative electroreductions of »difficult to reduce« organic compounds such as cyclohexanone. This conclusion may be precious, particularly in view of some advantages of working with a lead cathode (cost, facility of »scale up« etc.). The lead cathode really disappears although lead is reformed, but here this is not a disadvantage because a lead cathode can be reused many times.

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SAŽETAK

Svojstva i upotreba olovne katode kod vrlo negativnog potencijala

Z. Vajtner i M. Lukić

Istraživan je efekt više faktora na »katodnu koroziju« olova kao i na preparativnu redukciju cikloheksanona na olovnoj katodi: struja, gustoća struje, sastav elektrolita i čistoća olovne katode. Uspoređeni su rezultati preparativnih redukcija pri upotrebi živine i olovne katode pod inače identičnim uvjetima reakcije. Također su razmotreni odnosi rezultata »katodne korozije« i ukupne katodne reakcije za olovnu katodu. Pretpostavljeno je da se ukupna redukcija cikloheksanona uz opisane reakcijske uvjete sastoji od dvije kompetitivne reakcije: manjeg udjela direktnog prijelaza elektrona i dominirajućeg udjela indirektno redukcije s pomoću tetraalkilamonijum-olova.