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*Note*

# Reduction of Tetrabutylammonium Ion on Metal and Alloy Electrodes

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Metal cathodes can be categorized according to their reactivity with the tetrabutylammonium ion. It is demonstrated that an alloy (Wood's metal) cathode »corrodes« cathodically, producing »tetrabutylammonium metal« with significant reducing ability.

## INTRODUCTION

Organic electroreductions at very negative potentials are undoubtedly of significant interest in current chemistry.[1] Some time ago, we reported that, at very negative potentials, neither the tetraalkylammonium (TAA) cation (or cation like dimethylpyrrolidinium, nor some metal cathodes are inert.[2] In a solvent such as DMF they form »TAA metals« at the cathode surface, species with significant activity as mediators in some organic reductions. Properties and use of lead and tin cathodes were recently studied.[3-9]

We have focussed here on the investigations of an extended number of metal cathodes in order to determine whether it is possible to correlate the occurrence of this cathodic »corrosion« process with some physical properties of metals. We have separated the investigated metal cathodes into two groups: those reactive and those unreactive during reduction in the presence of tetrabutylammonium ion, according to their covalent radii and atomic volumes. The physical parameters mentioned above were chosen for comparison because only these values for the investigated metals differed significantly, depending on (in)activities of metals obtained experimentally. We believe, that publication of the work may urge other investigators choosing reactive metals to try to find the best conditions for electroreductions of organic compounds using solid metal cathodes, particularly in view of the advantages of using a solid cathode rather than a mercury cathode (cost, facility of »scale up« *etc.*).

We have also shown, for the first time, that an alloy such as Wood's metal will also »corrode« cathodically in the presence of tetrabutylammonium ion. Reporting the basic results of these experiments, we intend to focus on the great possibilities of work with this kind of relatively cheap cathode material.

## EXPERIMENTAL

Constant current reductions of tetrabutylammonium ion on metal cathodes were carried out under conditions chosen to repeat earlier investigations described in the literature.[2,7] A DMF (20 ml, Aldrich, HPLC grade) solution, containing 0.1 M tetrabutylammonium (TBA) tetrafluoroborate (Aldrich, 99%) as the supporting electrolyte, was electrolyzed at constant current (20 mA). Nitrogen was bubbled through the catholyte for 10 minutes prior to electrolysis and above it during the experiment. A divided cell was used, the amount of charge transferred was 36.0 C the temperature was 5 °C and the cathode surface was 4 $cm^2$. Metal cathodes (pure metal foils), as well as the Wood's metal cathode, were purchased from Aldrich. To determine whether the metal (alloy) surfaces had corroded (weight loss, $\Delta W$), the cathodes were washed with water and acetone, dried and weighted before and after electrolysis.

Cyclic voltammetry measurements were performed following the published procedure.[7] The working electrodes were pretreated by scanning the potential up to –3.0 V *vs.* SCE before each experiment.

## RESULTS AND DISCUSSION

Results of the constant current reductions are presented in Tables I and II. Metals that repeatedly show »cathodic corrosion« under experimental conditions described above are included in Table I, regardless of the extent of this corrosion. On the other hand, Table II presents the results for metals with no measurable weight loss and also no visible »corrosion« after electrolysis. These results show a correlation between the activity and covalent radius as well as atomic volume of elements.[10,11] It is clear that the covalent radii for the reactive metals are in the range 0.14–0.15 nm and significantly lower for the unreactive metals (Cd is an exception). Active metals with atomic numbers 49–51 and 80–83 are located in the 5$^{th}$ and 6$^{th}$ period[5], IIB–VB groups of the periodic system.

On the basis of the results mentioned above, we are sure that the size of covalent radius plays an important role in controlling the ability of the metal to participate in the process called »cathodic corrosion«, *i.e.* in the reaction with TAA ions such as tetrabutylammonium ion. But, it seems that the atomic volume of the metal is also an important parameter: reactive metals are those with atomic volumes of about 15.0–21.0. The value for the atomic volume of Cd (13.1) is probable sufficiently different so that the Cd cathode did not exhibit the expected activity (covalent radius 0.148 nm).

The next focus of interest in this work was to investigate the possibility of using an alloy such as Wood's metal (50% Bi, 25% Pb, 12.5% Cd, 12.5% Sn) at very negative

TABLE I

*Metal cathodes which react with the tetrabutylammonium ion*

| Metal (alphabetical) | Atomic number | Covalent radius (nm) | Atomic volume |
|---|---|---|---|
| Bi | 83 | 0.146 | 21.3 |
| Hg[a] | 80 | 0.149 | 14.8 |
| In | 49 | 0.144 | 15.7 |
| Pb | 82 | 0.147 | 18.3 |
| Sb[b] | 51 | 0.140 | 18.4 |
| Sn | 50 | 0.141 | 16.3 |

[a] Information from numerous reports, for example, Rf. 1.
[b] Ref. 2.

TABLE II

*Metal cathodes which do not react with the tetrabutylammonium ion*

| Metal | Atomic number | Covalent radius (nm) | Atomic volume |
|---|---|---|---|
| Al | 13 | 0.118 | 10.0 |
| Cd | 48 | 0.148 | 13.1 |
| Cr | 24 | 0.118 | 7.2 |
| Cu | 29 | 0.117 | 7.1 |
| Fe | 26 | 0.117 | 7.1 |
| Zn | 30 | 0.125 | 9.2 |

potentials. Figure 1 presents the results for the constant current electrolysis of 0.1 M tetrabutylammonium tetrafluoroborate in DMF using a Wood's metal cathode. The curve $\Delta W$ – charge is not a straight line, like in the case of electrolysis of pure metals,[7,9] that is, the different metals in the alloy react during electrolysis to form »TBA metals«. This suggestion is substantiated by visual inspection: at the start of electrolysis, formation is observed of dark rust and a dark blue »powder« (Sn, Bi), predominantly in the bulk. At the end of electrolysis, a dark precipitate is formed, predominantly at the cathode surface (Pb). Cyclic voltammograms at the Wood's metal electrode (electrolyte solution 0.1 M tetrabutylammonium tetrafluoroborate in DMF), compared with those

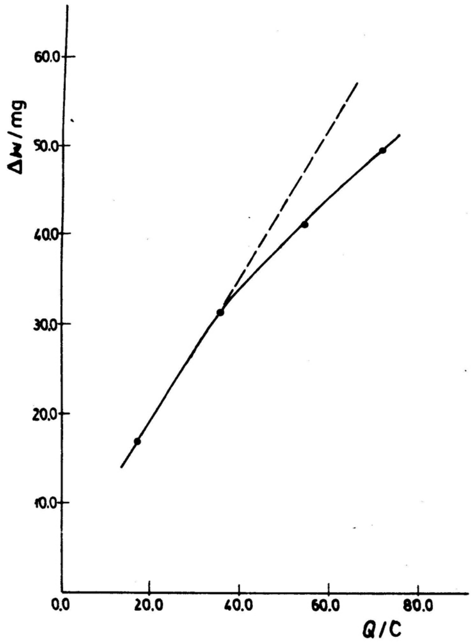


Figure 1. The graph shows »cathodic corrosion« for a Wood's metal cathode. The plot weight loss *vs.* charge passed in 0.1 M tetrabutylammonium tetrafluoroborate in DMF (20 ml), 5 °C, 5 mA cm$^{-2}$, cathode surface = 4 cm$^2$.

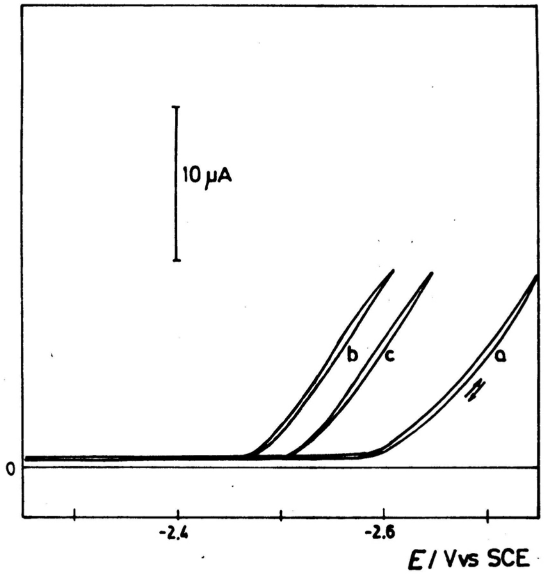


Figure 2. Cyclic voltammograms at Pb, Sn and Wood's metal electrodes, 0.1 M tetrabutylammonium tetrafluoroborate in DMF, 5 °C, d$E$/d$t$ = 20 mV $s^{-1}$.
a) Pb electrode, b) Sn electrode, c) Wood's metal electrode.

for Sn and Pb electrodes, show that Wood' s metal »corrodes« in a similar way to Sn (Figure 2). It can be noticed that, in the present paper, the alloy »corrosion« process was not compared to that of pure bismuth because the »cathodic corrosion« of this metal was not yet extensively investigated, except for the confirmation that bismuth shows a certain reactivity.[2] The product of electrolysis, »tetrabutylammonium – Wood's metal«, was tested by injecting 9-fluorenone or benzophenone into the cell, immediately after interruption of the current. The characteristic colors of the radical anions indicate the reducing properties of the electrolysis product.

Experiments are in progress to investigate the possibilities of using reactive metal and alloy cathodes in preparative reductions of some »difficult to reduce« organic compounds.

In summary, we have shown that it is possible to correlate the occurrence of the »cathodic corrosion« process of metal cathodes, in the presence of the tetrabutylammonium ion in a solvent such as DMF, with some physical properties of metals (covalent radii, atomic volumes). Metal cathodes can be categorized according to their reactivity with the tetrabutylammonium ion. It was also demonstrated, for the first time, that an alloy such as Wood' metal will also »corrode« cathodically in the presence of the tetrabutylammonium ion, producing »tetrabutylammonium metals« of significant reducing ability.

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## SAŽETAK

**Redukcija tetrabutilamonijeva iona na elektrodama iz metala i legura**

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Metalne katode mogu se razvrstati prema njihovoj reaktivnosti s tetrabutilamonijevim ionom. Prikazano je da i katode iz legure poput Woodova metala katodno »korodira«, dajući »tetrabutilamonijev metal« koji pokazuje značajna reduktivna svojstva.