

# *The nucleation of lead from halide-containing solutions*

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Received 24 February 1985; revised 16 April 1985

The density of active sites and the nucleation rates per site for the nucleation of lead onto vitreous carbon from lead ion solutions in the presence of halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) have been investigated. Mass transport to growing nuclei was not found to be affected by the formation of soluble complexes of lead with the halides. No systematic variation of the true nucleation rates per site was observed upon addition of halides to the electrolyte. The density of active sites for nucleation, on the other hand, increased in the presence of halides. It is also shown that, in the absence of halide ions, the density of active sites for the nucleation of both lead and silver are equal to and independent of the concentration of metal ions in solution.

## 1. Introduction

The electrodeposition of metals is a rather complex phenomenon, influenced by a number of factors that modify the rates of nucleation and growth and thus the final textures of the electrodeposits. Among the major factors affecting the nucleation process are the surface structure of the substrate, and effects induced by the specific adsorption of cationic, anionic or neutral species. Although it has long been known that the presence of adsorbing substances in electrolytic baths improves the quality of electrodeposits in general, the nature of their effects on the nucleation step has not been studied in detail as most of the work has been directed towards the understanding of the complexing reactions affecting the electrodepositing ion. Thus MacBrannen and Gannen [1] have studied the electrodeposition of zinc onto vitreous carbon electrodes from aqueous solutions in the presence of chloride and bromide ions and found that the nucleation overpotential was reduced in the presence of  $\text{Br}^-$  as compared to  $\text{Cl}^-$ , due to the smaller value of the stability constant of the complex  $\text{ZnBr}^+$  with respect to  $\text{ZnCl}^+$ . Morcos [2] has used similar arguments to explain the effects of cyanide ions on the

electrodeposition of silver. Nevertheless, none of these works have dealt with the effects of specific adsorption of the anions. A study of the electrochemical nucleation of silver onto vitreous carbon from EDTA-containing solutions [3] has shown that there exists a *reduction* of the density of active sites which cannot be associated with complexing of  $\text{Ag}^+$ . It was concluded that the adsorption of EDTA on the surface blocked active sites, preventing nucleation onto them. Vijn [4] studied the effects of halide ions on the electrodeposition of cadmium on copper and found that the cathodic polarization potential increased in the presence of halides in the sequence  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ , accompanied by a corresponding decrease in size of the cadmium crystals. Both adsorption of halides and complexing effects were put forward to explain the results.

In a recent paper it has been shown that both the density of active sites and the true nucleation rate per site can be obtained from the current maximum of single-step potentiostatic experiments [5]. This result was later applied in a study of the nucleation of lead on vitreous carbon [6], where it was found that the density of active sites was not dependent on the concentration of lead ions in solution although it varied

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with overpotential, whereas the nucleation rates were dependent of both concentration and overpotential.

In this paper, the electrochemical nucleation of lead onto vitreous carbon is studied from halide-containing solution in order to evaluate their effects on the nucleation rates and on the density of active sites on the surface.

## 2. Experimental details

The electrochemical cell, instrumentation and electrodes have been described elsewhere [6]. The reference electrode was a lead rod immersed in the same solution as in the working compartment in order to polarize the working electrode directly with respect to the equilibrium potential of metallic lead with its ions in solution, thus avoiding corrections to the reversible potential introduced by complex formation in solution. The potential differences applied between reference and working electrodes were thus the true overpotentials for the electrodeposition reaction. All solutions were prepared from triply distilled water and analytical grade reactants, used as received, except for  $\text{KNO}_3$ , which was recrystallized from triply distilled water. The concentration of lead ions in solution was kept at  $10^{-2}\text{M}$  throughout the experiments. The effects of  $\text{Cl}^-$  and  $\text{Br}^-$  were studied within the concentration range  $10^{-4}$ – $10^{-1}\text{M}$  while  $\text{I}^-$  was studied in  $10^{-5}$ – $10^{-3}\text{M}$  solutions, since the sparingly soluble salt  $\text{PbI}_2$  precipitated in more concentrated solutions. All solutions were balanced to a constant ionic strength of 1 M with  $\text{KNO}_3$ , used here as supporting electrolyte. The solutions were deoxygenated with a stream of argon between experiments.

Special care was taken in the preparation of the vitreous carbon electrode surface and in the application of the potential pulse trains, in order to maintain reproducible conditions to allow comparison of the electrode behaviour in the different solutions. The preparation method and pulse trains are described elsewhere [6]. Large amplitude anodic polarizations were avoided throughout this study, since these are known to increase the activity of the vitreous carbon surface towards nucleation [7].

## 3. Results and discussion

The typical response to the application of a train of potential pulses to the vitreous carbon electrode immersed in the working solutions is shown in Fig. 1. The long-time behaviour invariably showed that the current decayed to zero with  $t^{-1/2}$ , and that the mass transport of electrodepositing lead was not affected by the presence of halide ions in solution. The apparent diffusion coefficient of lead ions remained constant, disregarding the presence of halide ions at  $1.1 \times 10^{-5}\text{cm}^2\text{s}^{-1}$ , as previously reported [6]. This is in agreement with previous observations [8] that show that in solutions of  $\text{Pb}^{2+}$  in 0.1 M HCl the formation of the complex  $\text{PbCl}^+$  occurs and that its concentration is of the same order of magnitude than that of  $\text{Pb}^{2+}$ , but that their diffusion coefficients differ by less than 5%. Our observations then showed that, even though soluble complexes occur in solutions containing lead and halide ions, the mass transport of electrodepositing species is not significantly altered.

The nucleation of lead on vitreous carbon from the different solutions was thus studied from the current maxima [5]. The results

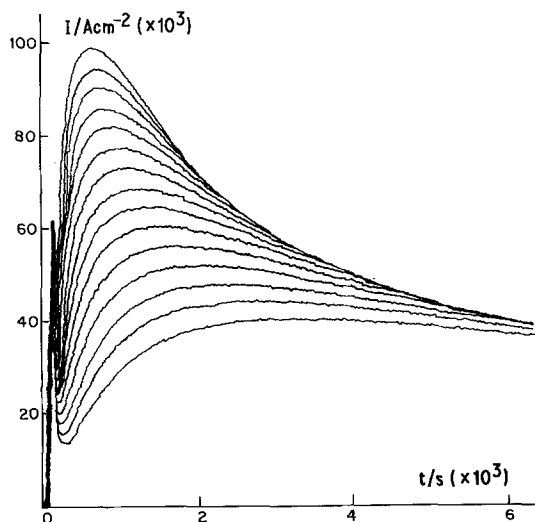


Fig. 1. Family of potentiostatic current transients corresponding to the nucleation of lead on vitreous carbon from a  $10^{-2}\text{M}$  solution of  $\text{Pb}(\text{NO}_3)_2$  in aqueous 1 M  $\text{KNO}_3$ . Overpotentials in the range 150–300 mV are plotted in increments of 10 mV.

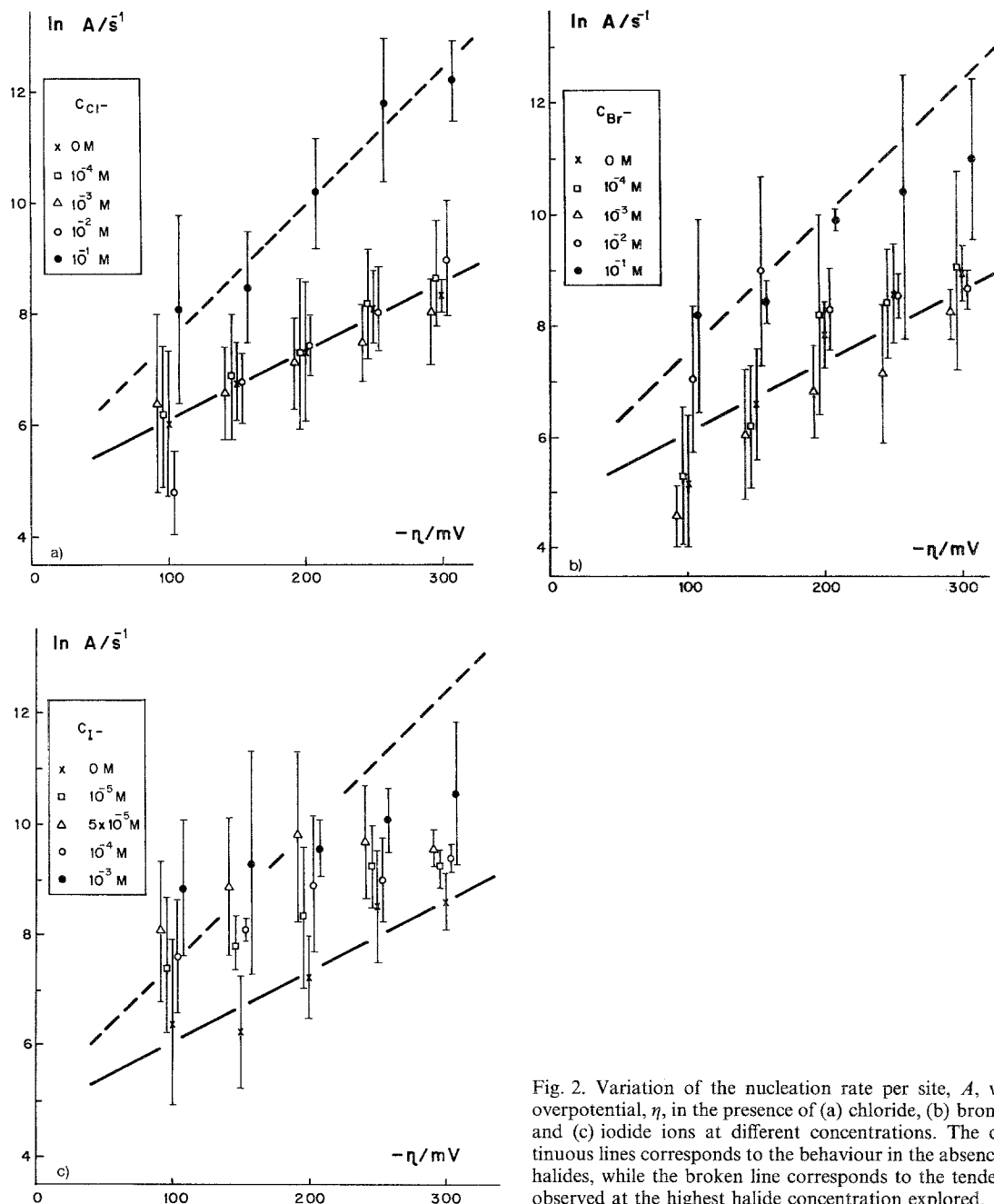


Fig. 2. Variation of the nucleation rate per site,  $A$ , with overpotential,  $\eta$ , in the presence of (a) chloride, (b) bromide and (c) iodide ions at different concentrations. The continuous lines corresponds to the behaviour in the absence of halides, while the broken line corresponds to the tendency observed at the highest halide concentration explored.

reported are the averages and standard deviations of five independent series of experiments for each concentration of halide ions. Three independent sets of five series of experiments were also performed in the absence of halide ions, to be used as blanks in the analysis of data.

The variation of the true nucleation rate of lead per site ( $A$ ) with overpotential ( $\eta$ ) in the presence of halide ions at different concentrations is shown in Fig. 2. Given the scatter of the data and that the standard deviations of different sets of data overlap in most cases, it is not possible to conclude the effects of the

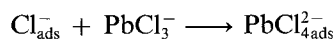
presence of halide ions on the true nucleation rates for lead. Nevertheless, in 0.1 M solutions of  $\text{Cl}^-$  and  $\text{Br}^-$ , an increase of  $A$  with respect to the blank solutions has been observed.

The plots of  $\ln A$  versus  $\eta$  are often used for the analysis of nucleation data according to the atomistic theory of nucleation. From the slopes of the lines in Fig. 2, the number of atoms forming the critical nuclei were evaluated and found to be invariably less than unity, indicating that the combination of an active site and a reduced lead atom on it may be regarded as a supercritical entity [9]. Even though important variations of the nucleation rates induced by the presence of halides in solution were not observed, the free energy of formation of the critical nuclei in the different solutions was evaluated. In order to calculate the free energy of formation of the critical nucleus within the framework of the atomistic theory, it is necessary that plots such as those in Fig. 2 show at least three linear regions over the overpotential range. As this was not observed in this system, the free energy of nucleation was evaluated according to the classical theory, improved by inclusion of the line tension effects [6]. This resulted in the free energy of formation of critical nuclei remaining invariant with overpotential or with the concentration of the different halides in solution. Thus we might conclude that even though the presence of halides may induce variations on the rates of nucleation of lead, it has little or no effect on the energetics (i.e. on the exponential term of the kinetic equations) of nucleation. This conclusion, however, should not be taken rigorously, given the extremely small size encountered for the critical nuclei [6, 10].

Fig. 3 shows the dependence of the density of active sites for lead nucleation ( $N_0$ ) with overpotential in the presence of chloride, bromide and iodide ions at different concentrations. In all cases, the density of active sites increases with overpotential, as we have previously reported for halide-free solutions [6]. Also, there is a tendency of  $N_0$  to increase in the presence of chloride and bromide ions. The effects of iodide ions are not as evident as those of the other halides studied, probably because solubility limitations dictated that its concentration had to be kept lower than the other halides. Thus, the

experimental evidence reported here indicates that the effects of halides on the nucleation of lead on vitreous carbon can be attributed mainly to an increase of the density of active sites on the surface, rather than to variations in the nucleation rates themselves caused by complexes involving lead ions in solution.

Complex formation, however, might play a role in the increase of the density of active sites on the surface. Sluyters-Rehbach *et al.* [11] have shown that lead adsorption occurs on mercury in the presence of chloride ions adsorbed on the surface, postulating the existence of soluble complexes of the type  $(\text{PbCl}_n)^{2-n}$  which, as the chloride concentration in solution is increased, are involved in surface reactions such as



thus promoting the adsorption of lead at the mercury-solution interface. Similar processes may take place at the vitreous carbon-solution interface and be responsible for the higher number of active sites for lead nucleation observed in solutions containing chloride and bromide ions as compared to the halide-free solutions. In this respect, MacKinnon *et al.* [12] have found that trace amounts of cadmium in chloride-containing solutions improve the quality of zinc electrodeposits on copper. This suggests that chloride might induce the adsorption of cadmium on the electrode, which then in turn acts as an active centre for zinc nucleation. The information available from this study does not allow for a detailed explanation of the surface phenomena involved. The adsorption of halides and/or  $\text{PbX}_n^{2-n}$  complexes *increases* the number of active sites, in contrast to observations in other cases (such as in the formation of oxides on noble metals) where the effect of the halides is to block the surface, thus *decreasing* the availability of sites for the formation of the new phase.

In the course of this study on the electrochemical nucleation of lead on vitreous carbon, much attention has been paid to the quantitative evaluation of the *number* of active sites on the surface. However, little knowledge has been gained about the *nature* of the active sites. Some fundamental questions still remain, such as whether the active sites are only characteristic of

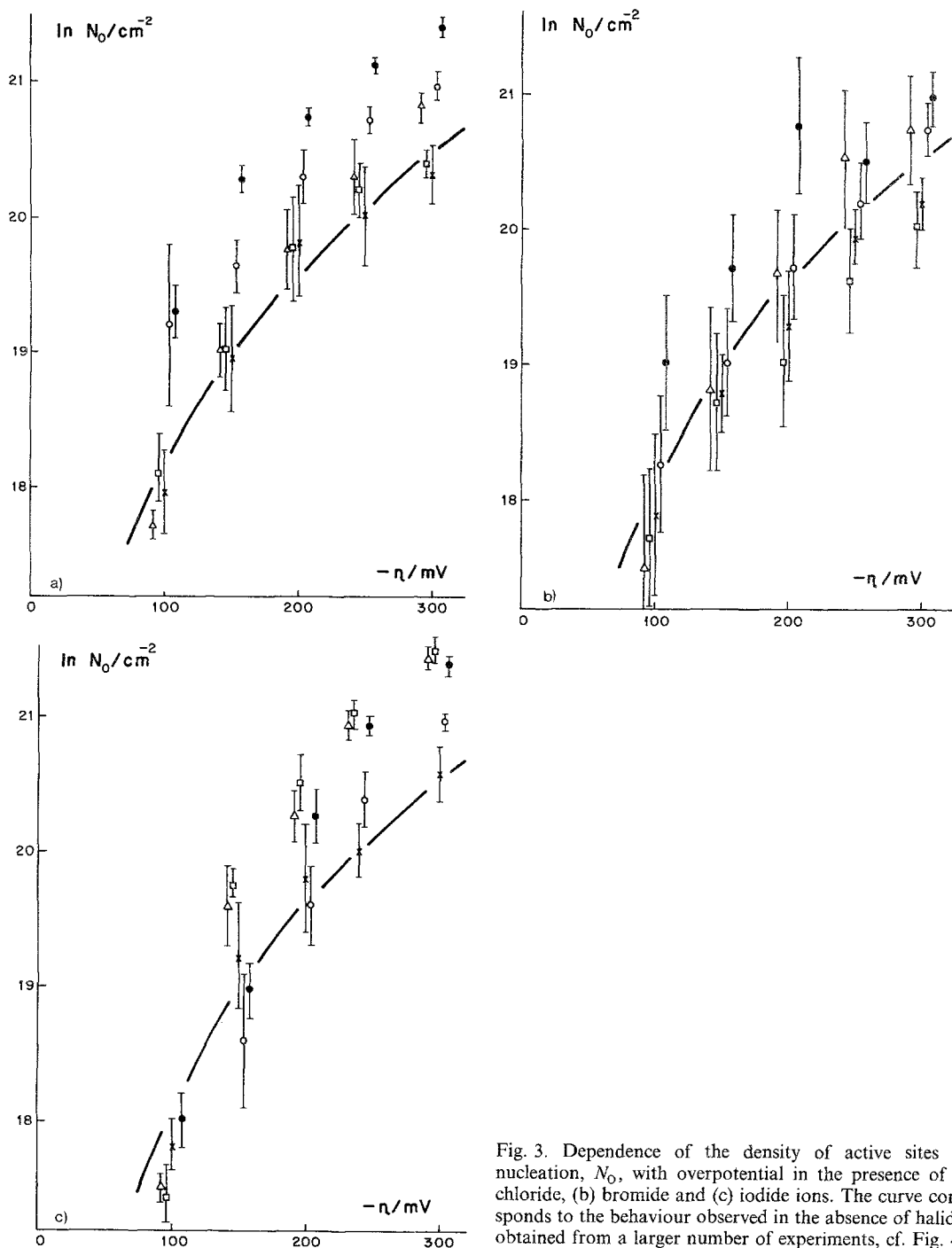


Fig. 3. Dependence of the density of active sites for nucleation,  $N_0$ , with overpotential in the presence of (a) chloride, (b) bromide and (c) iodide ions. The curve corresponds to the behaviour observed in the absence of halides, obtained from a larger number of experiments, cf. Fig. 4.

the electrode surface or, conversely, whether their activity depends on the metal being deposited. In a previous study [6], it was shown that the density of active sites for lead nucleation on vitreous carbon surfaces did not show a systematic dependence with the concentration of

lead ions in solution. In order to clarify whether the surface density of active sites for nucleation on vitreous carbon depend on the metal being deposited, the nucleation of silver onto the same electrode was investigated. Fig. 4 shows the density of active sites for silver nucleation on

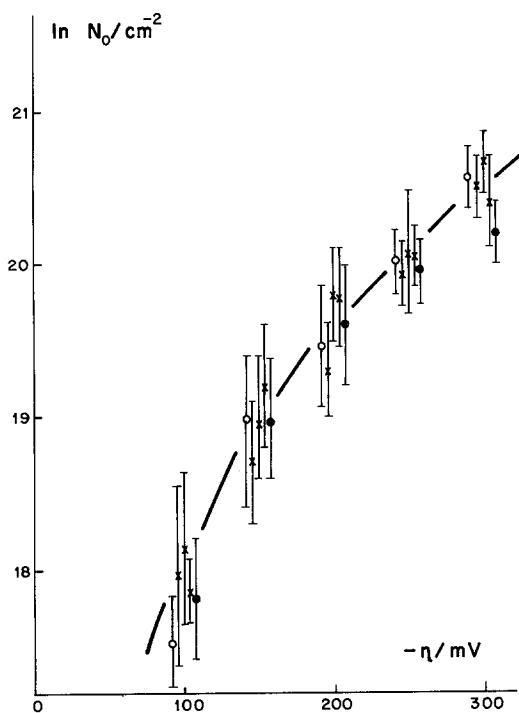


Fig. 4. Comparison of the density of active sites for silver nucleation from  $5 \times 10^{-3}$  (○) and  $20 \times 10^{-3}$  (●) M solutions of  $\text{Ag}^+$  with the density of active sites for lead nucleation from  $10 \times 10^{-3}$  M solutions of  $\text{Pb}^{2+}$  (×). The results of three independent sets of five experiments are shown for lead nucleation.

vitreous carbon from aqueous solutions of  $\text{Ag}^+$  at two different concentrations. The density of active sites for lead nucleation from 10 mM solutions of  $\text{Pb}^{2+}$  in the absence of halides is also shown for comparison. It can be observed that  $N_0$  does not differ significantly from one case to the other, thus indicating that the vitreous carbon electrode, under identical conditions of surface preparation, offered a similar number of active sites towards the nucleation of both lead and silver. Given the difference in molar charge between the electrodeposition reactions, and given that the free energy of formation of the bulk material can be defined as the product of the net charge of formation of the cluster and the applied overpotential, then, at one and the same overpotential, the bulk free energy of formation of lead is twice that of silver. Since the size of critical nuclei of lead [6] and silver [9] are comparable and nearly zero within the overpotential range covered in Fig. 4, it follows that the thermodynamic work for nucleus formation

approaches zero in both cases and therefore that only the kinetics determine the phase formation. Thus, at the high supersaturations imposed throughout this study, the active sites may be regarded as places on the surface where the residence time of adatoms is increased with respect to other sites on the surface. Still, their precise nature remains obscure [9].

#### 4. Conclusion

The apparent diffusion coefficient of lead ions is not changed by the formation of soluble complexes with halides. Thus, mass transport to the electrode surface remains invariant upon addition of halides to the electrolytic solution.

A systemic variation of the true nucleation rates of lead on vitreous carbon upon addition of halides to the electrolyte was not observed. The density of active sites for nucleation, on the other hand, increases in the presence of halides. Finally, it was shown that under identical conditions of surface preparation, the density of active sites for the nucleation of both lead and silver are similar.

#### Acknowledgement

Financial support from the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT), Venezuela, through Grant No. S1-1227 is gratefully acknowledged.

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